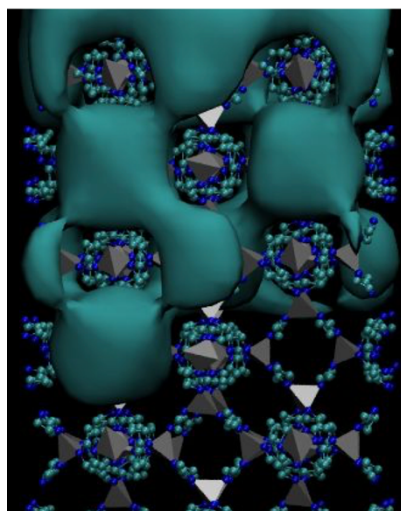


Fluids in porous materials: From fundamental physics to engineering applications



June 19 - 21, 2023
CECAM-HQ-EPFL, Lausanne, Switzerland

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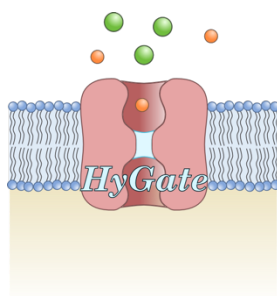
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1. Description

Liquid intrusion in nanoporous systems (“**wetting**”) is the process by which the fluid replaces the pre-existing vapor/gas phase present in the medium. **Extrusion** (“**drying**”) is the opposite process. For long time, the theoretical description of intrusion/extrusion has been based on the capillary theory of multiphase systems (see, e.g., Ref. [1]). During the last 10-15 years, some progress has been made developing rigorous statistical mechanics approaches describing intrusion/extrusion as a rare event (see, e.g., [2]). Among other advancements, this led to the discovery of unconventional wetting paths of cavities that could explain some experimental results, but also highlighted mismatches with the empirical evidence [3]. This suggested that the quasi-static description of the intrusion/extrusion process one obtains with well-established simulation techniques may be insufficient [4]. Moreover, novel (sub)nanoporous materials attracted the interest of experimentalists, adding significant theoretical challenges: i) they cannot be described by continuum models, ii) are highly flexible, iii) might change configuration during the process (e.g., biological channels), iv) present shallow interconnected pores defeating classical Cassie-Baxter/Wenzel behavior, v) present an unusually low intrusion pressure, etc. Related problems and challenges are also encountered in the processes of solvent evaporation from nanoporous materials.

Nanoporous materials immersed in liquids are promising for their potential applicability to develop novel technologies. In some cases, intrusion/extrusion may be accompanied by other phenomena, such as triboelectrification and heat flow, which call for a comprehensive description of these processes and make them potentially usable to scavenge low-grade energy available in the environment. The peculiar behavior of water in nanopores is central also for several phenomena of biomedical interest, including selectivity, conduction, and gating mechanisms of ion channels [1], which can serve as a source of inspiration for technologies for water purification, nanopore sensing, nanofluidic circuits, and drug delivery. Understanding the physical origin of these properties and developing quantitative tools to engineer them is the key for the progress of nanopore-based technologies.

Understanding intrusion/extrusion/evaporation in system with complex chemistry and topology, and their combination with other phenomena is still in its infancy. The objective of this workshop is to gather experimentalists and theoreticians to discuss fundamental and technological aspects of these processes, including:

1. Fundamental questions on the intrusion/extrusion/evaporation mechanism, energetics, and kinetics in complex porous systems: disordered grafted porous systems, metal- or covalent-organic framework, porous polymeric materials [5], soft porous media – biological channels. This includes, for example, how liquid penetrates in porous materials - e.g., via condensation or via a cascade advancement? – and its dependence on the morphological characteristics of the porous media – e.g., cage-like vs channel-like systems – and their chemical nature – e.g., hydrogen bonding with some atoms of the material.
2. Challenges in the simulation of intrusion/extrusion/evaporation: quasi-static (e.g., string method) vs “dynamical” methods (e.g., transition interface sampling), and multiscale aspects in time and space in general.
3. Challenges in the experimental investigation of intrusion/extrusion/evaporation: *in situ* structural measurements, heat flux, charging/discharging of the liquid/solid interface, ionic conduction across nanopores, stability of ultrathin liquid films.
4. Identify possible novel technological applications of these systems and establishing collaborations among the participants to tackle them.

Key References

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- [4] S. Marchio, S. Meloni, A. Giacomello, C. Casciola, *Nanoscale*, **11**, 21458 (2019)
- [5] D. Wu, F. Xu, B. Sun, R. Fu, H. He, K. Matyjaszewski, *Chem. Rev.*, **112**, 3959 (2012)

2. Program

Day 1 - Monday June 19th 2023

- 13:30 to 14:00 - Welcome & Introduction
- 14:00 to 14:30 - **Frédéric Caupin**
Liquid-vapor equilibrium in a closed system and application to palaeotemperature reconstruction
- 14:30 to 15:00 - **Patrick Huber**
Water confined in nanopores: What do we know about it and what is it good for?
- 15:00 to 15:30 - Coffee break
- 15:30 to 16:00 - **Benjamin Rotenberg**
From ion adsorption in nanoporous carbon electrodes and electrokinetic transport through nanotubes to blue energy harvesting and desalination
- 16:00 to 16:30 - **Amaël Obliger**
Non-fickian effects on desorption from source rocks' organic matter
- 16:30 to 17:00 - **Luis Bartolomé**
Intrusion-extrusion of non-wetting liquids into/from nanopores: Triboelectrification
- 17:00 to 18:00 - Posters/discussion (with some beers)

Day 2 - Tuesday June 20th 2023

- 09:00 to 09:30 - **Peter Bolhuis**
Elucidating phase transition mechanisms with path sampling
- 09:30 to 10:00 – **Roland Roth**
- 10:00 to 10:30 - **Antonio Tinti**
Intrusion and extrusion of nonwetting liquids in nanopores, a perspective from molecular simulations.
- 10:30 to 11:00 - Coffee break
- 11:00 to 11:30 - **Yueting Sun**
Mechanical energy absorption of metal-organic frameworks
- 11:30 to 00:00 - **Cyril Picard**
From wetting and drying dynamics in hydrophobic nanopores to volume swing osmosis to harvest osmotic energy
- 12:00 to 13:30 – Lunch

- 13:30 to 14:00 - **Alexander Neimark**
Mesocanonical ensemble Monte Carlo (MCeMC) simulations of phase transitions in nanoconfined fluids
- 14:00 to 14:30 - **Andriy Yaroshchuk**
Time-resolved pressure-induced potential in nanoporous materials: Measurements, interpretation and some implications for understanding fluid properties in nanopores
- 14:30 to 15:00 - **Gonalo Paulo**
- 15:00 to 15:30 - Coffee break
- 15:30 to 16:00 - **Benoit Coasne**
Bridging molecular dynamics and macroscopic transport in nanoporous materials
- 16:00 to 16:30 - **Mykola Isaiev**
Features of thermal transport in nanoporous hybrid media
- 16:30 to 17:00 - **Josh David Littlefair**
Revealing the cage-by-cage mechanism of liquid water intrusion into porous solids
- 17:00 to 18:00 - Posters/discussion
- 19:00 to 00:00 - Social Dinner

Day 3 - Wednesday June 21st 2023

- 09:00 to 09:30 - **Jin-Chong Tan**
Fundamentals of MOF mechanics & structure-mechanical property relationships
- 09:30 to 10:00 - **Daniela Secci**
Metal-organic frameworks (MOFs) as biomolecules drug delivery systems for anticancer purposes
- 10:00 to 10:30 - **Mikhail Suetin**
Investigating the separation of propane/propylene by utilizing molecular dynamics simulations on model of flexible metal-organic frameworks
- 10:30 to 11:00 - Coffee break
- 11:00 to 11:30 - **Richard Remsing**
Surprising effects of vacancies on surface hydrophobicity
- 11:30 to 00:00 - **Olivier Vincent**
Water and solutions in nanoporous media: Capillarity, osmosis and phase change
- 00:00 to 13:30 - Lunch
- 13:30 to 14:00 - **Andrey Ryzhikov**
High pressure intrusion of aqueous salt solutions in hydrophobic zeolites
- 14:00 to 14:30 - **Pietro Asinari**
Understanding mass transport in reactive porous materials for advanced energy storage

- 14:30 to 15:00 - **Paolo Guglielmi**
Drug loaded metal-organic frameworks conjugated with monoclonal antibody for antitumoral purposes
- 15:00 to 15:30 - Coffee break
- 15:30 to 16:00 - **Elisabeth Charlaix**
- 16:00 to 16:30 - Conclusions

3. Abstracts

Bridging molecular dynamics and macroscopic transport in nanoporous materials

Benoit Coasne¹, Wanda Kellouai², Jean-Louis Barrat², Colin Bousige³, Pierre Levitz⁴

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Nanoporous materials (pore size 1 – 100 nm) are at the heart of numerous important applications: adsorption (e.g., gas sensing, chromatography), energy (e.g., hydrogen storage, fuel cells and batteries), environment (e.g., phase separation, water treatment, nuclear waste storage), etc. Among these materials, nanoporous solids which have pores \lesssim nm (e.g., active carbons, zeolites), are particularly interesting as ultraconfinement in their porosity leads to novel adsorption and transport phenomena. In this talk, we will present how statistical physics allows developing models for adsorption and transport in these extremely confining materials (1,2). We will see how simple thermodynamic modeling allows rationalizing adsorption by considering reminiscent capillarity at vanishing lengthscales. Then, we will show how transport in subnanoporous media can be described without having to rely on macroscopic concepts such as hydrodynamics (3,4,5). In particular, using parameters and coefficients available to experiments, we will see how transport coefficients can be rigorously upscaled using simple models such as free volume theory (3), intermittent Brownian motion (5), De Gennes narrowing (6), etc. If time allows, we will also consider the confinement of fluids in metallic nanoporous materials which has received far less attention compared to insulating materials (7).

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[6] W. Kellouai et al., *To be submitted* (2023)

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Coarse-graining wetting and drying in hydrophobic nanoporous materials: Temperature, cycling speed and the role of interconnections.

Gonçalo Paulo

Sapienza University of Rome, Italy

Understanding intrusion and extrusion in nanoporous materials is a challenging multiscale problem, and including atomistic details in simulations is required to predict the dynamics of these processes. On the other hand, the transitions between the filled (intruded) and empty (extruded) states are rare events that often require long simulation times, which are difficult to achieve with standard atomistic simulations. We will look at a multiscale approach, using Restrained Molecular Dynamics to extract the free energy associated with the wetting and drying of two nanoporous systems. In a simple model hydrophobic nanopore we use Langevin dynamics to reproduce experimentally relevant features such as the time and temperature dependence of the intrusion/extrusion cycles, as well as specific details about the shape of the cycle. To finalize the talk, we look at a more complex nanoporous structure, with subnanometric connections between pores, and find that surprisingly these channels get wet. We use the same free energy techniques to predict the intrusion and extrusion behavior of these model material, and find that these subnanometric connections, which are normally ignored while considering the intrusion and extrusion properties, do in fact matter.

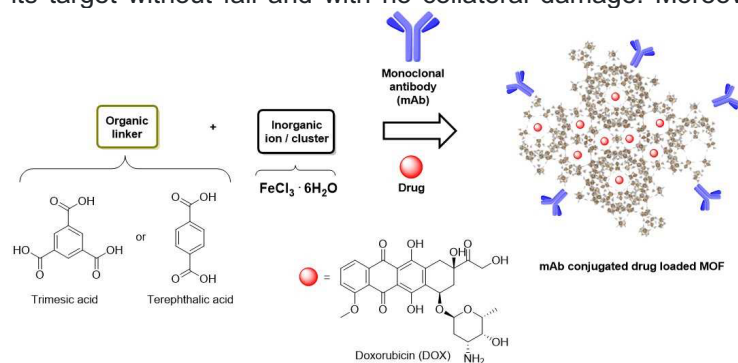
[1] G. Paulo, A. Gubbiotti, A. Giacomello, *The Journal of Chemical Physics*, **158** (2023)

[2] G. Paulo, A. Gubbiotti, Y. Grosu, S. Meloni, A. Giacomello, *Commun. Phys.*, **6**, 21 (2023)

Drug loaded metal-organic frameworks conjugated with monoclonal antibody for antitumoral purposes

Paolo Guglielmi, Michele Coluccia, Daniela Secci
Sapienza University of Rome, Italy

Metal-organic frameworks (MOFs) are porous crystalline solids occurring by the assembly of organic linkers and inorganic ions or clusters. These materials are endowed with impressive surface area and by selecting the proper inorganic core, ligands and synthetic conditions, their properties can be finely tuned [1]. Metal-organic frameworks have been extensively investigated for many purposes spanning from absorption and separation of gaseous molecules to biomedical application. In particular, different MOFs have been developed with the aim to obtain novel drug delivery systems able to load high number of drugs. Moreover, some systems are sensitive to external (temperature, magnetic field, light, ultrasound) or internal (pH, temperature, oxidative-state cell conditions) stimuli, that can be exploited to selectively trigger the drug release on the specific sites. In this regard, another opportunity to address the MOF against targets is by conjugating these systems with monoclonal antibody, that are extremely selective for specific epitopes expressed by cells in different pathologies [2]. Here I report the system developed by our research group, based on MOF loaded with antitumoral drug and conjugated with monoclonal antibody in order to obtain the “magic bullet” originally described by Paul Ehrlich as a drug able to hit its target without fail and with no collateral damage. Moreover, I will describe the design, synthetic approach, and the characterization data for this drug delivery system (Figure 1). Metal-organic frameworks (MOFs) are porous crystalline solids occurring by the assembly of organic linkers and inorganic ions or clusters. These materials are endowed with impressive surface area and by selecting the proper inorganic core, ligands and synthetic conditions, their properties can be finely tuned [1]. Metal-organic frameworks have been extensively investigated for many purposes spanning from absorption and separation of gaseous molecules to biomedical application. In particular, different MOFs have been developed with the aim to obtain novel drug delivery systems able to load high number of drugs. Moreover, some systems are sensitive to external (temperature, magnetic field, light, ultrasound) or internal (pH, temperature, oxidative-state cell conditions) stimuli, that can be exploited to selectively trigger the drug release on the specific sites. In this regard, another opportunity to address the MOF against targets is by conjugating these systems with monoclonal antibody, that are extremely selective for specific epitopes expressed by cells in different pathologies [2]. Here I report the system developed by our research group, based on MOF loaded with antitumoral drug and conjugated with monoclonal antibody in order to obtain the “magic bullet” originally described by Paul Ehrlich as a drug able to hit its target without fail and with no collateral damage. Moreover, I will describe the design, synthetic



approach, and the characterization data for this drug delivery system (Figure 1).

Figure 1. Scheme of the drug delivery system developed.

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Elucidating phase transition mechanisms with path sampling

Peter Bolhuis

University of Amsterdam, Netherlands

Phase transitions often take place by nucleation: the formation of the stable phase into the metastable parent phase. The nucleation process is qualitatively described by classical nucleation theory. However, the pertinent reaction coordinates describing (crystal) nucleation are still poorly understood, in particular for complex systems. Enhanced sampling can help to better understand and predict this process. Transition path sampling and transition interface sampling allow estimate the rate constants, and explore the mechanism, without any dynamical bias.

I will discuss applications on Lennard-Jones liquids, colloidal fluids, and methane hydrates. In the latter case, there is a large influence of the geometry of the liquid-gas interface on the nucleation barrier and rate, of possible relevance for (nano)porous materials.

Features of thermal transport in nanoporous hybrid media

Mykola Isaiev

LEMTA, CNRS (UMR 7563), Université de Lorraine, France

Nanoporous hybrid systems formed by porous matrix filled with liquid are frequently employed for energy storage and conversion. Overheating and hotspots arising started to be a real bottleneck for the efficiency and stability of the devices based on those types of media. Therefore, the management of thermal transport is crucial for designing such nanocomposite systems. This thermal engineering requires a clear understanding of the phenomena connected with interfacial thermal transport across the solid/liquid interface.

During the talk, the experimental results concerning features of thermal transport properties of nanoporous silicon filled with a viscous liquid will be presented. Such results state the interfacial layer's significant impact on the effective thermal conductivity of the nanocomposite. Furthermore, molecular dynamics simulations were performed to give insight into understanding the interfacial layer's role in significantly enhancing the thermal transport of nanocomposite compared to the pristine porous matrix.

From ion adsorption in nanoporous carbon electrodes and electrokinetic transport through nanotubes to blue energy harvesting and desalination

Benjamin Rotenberg

CNRS and Sorbonne Université, France

Osmotic or "blue" energy, arising from the salinity difference between two solutions such as sea- and river water, has been identified as a potential source of renewable and non-intermittent energy several decades ago. The first attempts at harvesting the mixing free energy that is otherwise dissipated as heat in estuaries were based on membrane-based technologies, such as pressure-retarded osmosis and reverse electrodialysis. Conversely, it is also possible to spend energy to desalinate water using membranes. In recent years, alternative processes have been proposed, which rely on different physical mechanisms also involving fluids confined at the nanoscale, but are less hindered e.g., by the dissipation arising from fluid flow through extremely narrow pores. In this presentation, I will report some contributions of molecular simulations to the understanding and modelling of ion adsorption through nanoporous carbon electrodes and to electrokinetic transport through carbon or hexagonal boron nitride nanotubes, in the contexts of blue energy harvesting by Capacitive Mixing or diffusio-osmosis, respectively. I will in particular discuss how the molecular insights can be related to the continuous descriptions used to interpret experiments or make predictions in these contexts.

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From wetting and drying dynamics in hydrophobic nanopores to volume swing osmosis to harvest osmotic energy

Cyril Picard, Xavier Cattoen, Elisabeth Charlaix
Université Grenoble Alpes, France

The forced intrusion and spontaneous extrusion of water in hydrophobic nanopores to store and retrieve mechanical energy, started a very active field of research. One particularly intriguing feature of these systems is their excellent dynamical response, which makes them of interest for the quick storage of mechanical energy. From a fundamental point of view, these systems make a direct bridge between dynamical phenomena at stake within nanopores and the time dependance of measurable bulk quantities such as pressure. These systems give the ability to probe and characterize experimentally, dynamical wetting and drying in nano [1,2] or even angstrom-confinements. In this presentation we will share experimental results obtained with several hydrophobic nanoporous materials that demonstrate various behaviors. Although partly explained, these quick filling and drying processes can be leverage not only for energy storage, but also for novel energy conversion means. Selective hydrophobic nanoporous particles [3] may be used to harvest the osmotic energy associated to free enthalpy of mixing of two electrolytes solutions of different concentrations. Its conversion to useful mechanical work or electricity has the potential to be a source of renewable energy commonly called blue energy in the case of mixing of river water with sea water. The remarkable development of membrane technology has opened new perspectives to harvest this osmotic energy. However, the establishment of several prototypes has resulted in the identification of some strong limitations in membrane-based approaches, such as concentration polarization. Inspired from the pressure swing adsorption process, well known for gas separation, we propose a membrane-free method to recover osmotic energy based on osmosis between the inside and the outside of hydrophobic nanoporous sieve. This Volume Swing Osmosis approach [4] operates as a cycle which takes benefit from both intra-particle and inter-particle porosities as well as the natural resistance of particles to high pressure [5]. It relies on alternating intrusion/extrusion processes with concentration changes of the liquid around the particles. I will present the principle of this process and if time allows the prototype currently built in the lab to illustrate it.

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Fundamentals of MOF mechanics & structure-mechanical property relationships

Jin-Chong Tan

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Hybrid nanoporous materials known as “metal-organic frameworks” (MOFs) have attracted considerable interests from the scientific and industrial sectors by virtue of their enormous structural, chemical, and functional possibilities. Potential applications include sensors, photoluminescence [1], molecular separations and catalysis, and more recently it has been shown that energy conversion [2] and mechanical energy absorption [3-4] are highly promising by leveraging the unique mechanical response of porous MOF structures. In this talk, I will focus on the basic principles underscoring the mechanical performance of MOF materials, the new science we termed “MOF Mechanics” [5], which may explain many of the unexpected guest uptake-release characteristics observed. The elastic, yielding/plastic, interfacial adhesion and fracture toughness of prototypical MOF-type materials will be elucidated, this will encompass single crystals, bulk monoliths, thin films and composite membranes. Furthermore, I will touch on the Terahertz framework dynamics, soft modes, and shear deformation mechanisms omnipresent in MOFs, which affect framework functions and could mechanically destabilize the extended framework structure. Finally, Ashby-style material selection charts [5] are presented employing the latest data found in the literature, unravelling the interesting trends and vast opportunities in the field of MOF mechanics [6].

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High pressure intrusion of aqueous salt solutions in hydrophobic Zeolites

Andrey Ryzhikov, T. Jean Daou, Habiba Nouali, Amir Astafan, Gérald Chaplais
 Institut de Science des Matériaux de Mulhouse (IS2M), France

High pressure intrusion of non-wetting liquids in porous solids is a promising way to absorb and store mechanical energy. The systems based on hydrophobic pure silica zeolites (Zeosils) and water or aqueous electrolyte solutions are studied for these applications. The use of aqueous salt solutions allows to improve the energetic performance of such systems in comparison with water by a significant increase of intrusion pressure. In this talk, we present our studies on the influence of Zeosil structure, electrolyte nature and concentration on intrusion-extrusion characteristics of aqueous salt solutions. It has been shown that the rise of intrusion pressure with salt concentration is more pronounced for the channel-type zeolites with small pore openings, however no clear trend is observed for the cage-type ones. A relative increase of intrusion pressure in comparison with water is particularly strong for the Zeosils with narrow pore openings. The use of highly concentrated aqueous solutions instead of water can lead to a change of energetic behavior of Zeosil-based systems that seems to be related to a lower formation of silanol defects under intrusion of solvated ions and a weaker interaction of the ions with silanol groups of Zeosil framework [1].

It has been also shown that the nature of anion has a drastic influence on the behavior of Zeosil-based systems that can be related to the affinity of the ions to Zeosil framework. Its considerable influence on intrusion pressure has been also observed [2]. The nature of cation has a slight impact on systems behavior, but a strong influence on intrusion pressure. The pressure increases with the cation diameter decrease for alkaline and alkali-earth metals. In the same way, the increase of cation charge leads to a pressure rise. These trends are also in agreement with cation hydration enthalpy values.

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Intrusion and extrusion of non-wetting liquids in nanopores, a perspective from molecular simulations

Antonio Tinti

Sapienza University of Rome, Italy

Intrusion and Extrusion of nonwetting liquids in nanopores are nowadays an established field of investigation, owing to the fundamental interest and the technological applications that are associated to these peculiar applications of nanoporous materials.

Intrusion and Extrusion processes can be briefly summarized by noticing how, upon compression liquids can be made to intrude the naturally dry matrix of pores of a hydrophobic nanoporous material. Conversely, by reducing the pressure of the container it is possible to induce the nucleation of vapor inside the pore confines ultimately leading to the dewetting of the matrix and the extrusion of water from the pores.

From the theoretical point of view intrusion and extrusion processes appear as the ideal testbed to gauge the limits of capillary theories with the inclusion of nanoscale effects such as line tension, along with the effect of confinement on the phase behavior of simple liquids.

From an engineering perspective nanoporous systems subject to liquid intrusion/extrusion show great promise as mechanical energy dissipation and storage devices, but they also show great promise in other fields such as the storage of chemicals, catalysis and other nanofluidic applications.

Objective of this talk is to offer a wide perspective of the insight that advanced molecular simulations have been offering on this fascinating problem over the last few years, and to offer a comparison with the atomistic results with the predictions of classical capillarity.

More in particular we will discuss the fundamental mechanisms of liquid intrusion and extrusion, along with providing microscopic insight over the role of dissolved gases and ions. Upcoming results will also be discussed, detailing the impact of silane grafting over the intrusion/extrusion phenomenology.

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Intrusion-extrusion of non-wetting liquids into/from nanopores: Triboelectrification

Luis Bartolomé, Yaroslav Grosu
CIC energiGUNE, Spain

Among the civilization-scale challenges for the next decades, reducing greenhouse gas emissions and pollution needs to be resolved urgently. In addressing this challenge, rational energy use is a crucial component, where the conversion of waste heat and vibrations into useful electricity would be a promising approach. In this presentation, we demonstrate how the intrusion-extrusion process of non-wetting liquids into-from nanoporous materials can be used to convert environmental heat and mechanical energy of vibrations into useful electricity via triboelectrification. [1,2] The electro-intrusion approach is applicable to mechanical and/or thermal energy harvesting applications where excess energy is wasted, e.g., transport shock-absorbing, walking and body movement, vibrations of domestic appliances, etc. Electrification experiments of water intrusion-extrusion into/from superhydrophobic materials, such as C8 grafted silica and ZIF-8 Metal-Organic Framework (MOF), are presented to demonstrate this concept, in particular, these experimental findings are discussed within the framework of Horizon 2020 Electro-Intrusion [3] project dedicated to these phenomena.

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Investigating the separation of propane/propylene by utilizing molecular dynamics simulations on model of flexible metal-organic frameworks

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The separation of chemical mixtures into pure forms is a complex and energy-intensive process that currently accounts for up to 15% of the world's energy consumption. Unfortunately, this process also contributes significantly to climate change. However, metal-organic frameworks (MOFs) offer a promising solution to this challenge. MOFs are porous crystalline materials with diverse applications in fields such as light harvesting, memory nanodevices, drug delivery, biomedical imaging, supercapacitors, water harvesting, catalysis, and gas storage and separation. Due to their modular crystalline structure, MOFs are particularly well-suited for separating molecules with similar physicochemical properties. Therefore, they have gained increasing attention in recent years as a potential solution for the separation of hydrocarbons, including propane and propylene.

In this talk, I will focus on the computational screening of MOF structures from the Computation-Ready Experimental Metal-Organic Framework (CoRE MOF) 2019 Dataset using classical molecular dynamics simulations. MOFs are treated as flexible structures. The goal of this study is to identify materials with strong potential for separating propane and propylene via diffusion. By taking into account the impact of framework flexibility on the discovery of guest diffusion coefficients, this study underscores the importance of considering framework flexibility in investigations of gas molecule transport in MOFs. Moreover, this study showcases the potential of using data-driven approaches to identify high-performance materials and suggests methods for enhancing the predictive capabilities of screening workflows. Finally, I will present some machine learning approaches that can be used to predict diffusion coefficients.

Liquid-vapor equilibrium in a closed system and application to palaeotemperature reconstruction

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When a fluid is constrained to a fixed, finite volume, the conditions for liquid–vapor equilibrium are different from those for the infinite volume or constant pressure cases. There is even a range of densities for which no vapor bubble can form, and the liquid at a pressure below the bulk saturated vapor pressure remains indefinitely stable [1,2]. These effects, caused by surface tension, become more pronounced when the system becomes more confined. Sizeable changes are observed even for volumes around 10 μm . We provide a simple, largely analytic, theory to account for this phenomenon [3]. The results are applied to fluid inclusions in salt crystals. The temperature at which a bubble disappears in these objects is used to retrieve the temperature at which they were formed, with implications for reconstructing past temperatures [4,5]. Our model shows that a correction of around 1 °C needs to be applied, which indeed restores agreement between temperature reconstruction and direct observations.

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Mechanical energy absorption of metal-organic frameworks

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Development of energy absorption materials and structures is required for improved protection from damages and injuries associated with mechanical impact, vibration, or explosion. These can be seen in many fields such as vehicle crash safety, anti-blast body armor or armored vehicles, vibration-proof precision equipment, earthquake-resistant building structures, and sports products such as helmets. However due to the limitation of conventional mechanisms in efficiency, reusability, and controllability, there is a pressing need to discover new science of energy absorption. Recently nanoporous materials are finding their applications in this area. The high surface area and porosity offered by materials like metal–organic frameworks (MOFs) can be exploited to absorb mechanical energy via solid–liquid interactions or framework deformations [1]. For example, the pressurized intrusion of non-wetting liquid into MOF nanopores can absorb mechanical energy and mitigate impact by generating a large solid–liquid interface [2,3]. This talk will provide an overview of energy absorption of nanoporous materials, and discuss the recent development of pressurized liquid intrusion of MOFs from quasi-static to highly dynamic regime [2], including the investigations of materials in different forms, behaviors at different mechanical and environmental conditions, and their potential applications.

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Mesocanonical ensemble Monte Carlo (MCeMC) simulations of phase transitions in nanoconfined fluids

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Phase behavior of fluids confined in nanopores is affected by geometric constraints and extensive guest-host interactions. In many systems, nanophase transitions are associated with enduring metastable states and hysteretic transitions. The defining features of nanophase transitions are well documented in gas adsorption-desorption and nonwetting fluid intrusion-extrusion experiments with micro- and mesoporous materials such as silica, zeolites, and MOFs. The mesoscopic canonical, or mesocanonical, ensemble (MCE) is devised to study the nanophase behavior under conditions of

controlled fluctuations that allows to stabilize metastable and labile states. In the MCE, the system of interest (a nanopore, or a system of nanopores) is considered in equilibrium with a gauge cell of limited volume. The volume of this gauge cell controls the allowable density fluctuations in the confined fluid. In this respect, the MCE is a middle ground between the grand canonical ensemble (GCE), which permits unlimited fluctuations and the canonical ensemble (CE), which considers a close system. Gauge cell MCCEM simulations produce van der Waals type, S-shaped isotherms with distinctive swings around the phase transitions regions. The constructed isotherms determine the positions of phase equilibrium using the Maxwell rule, the spinodals, and the nucleation barriers of phase transitions. By using various examples of gas adsorption on nanoporous materials, I will demonstrate the advantage of the MCCEM method over standard GCEM and CEMC methods. This advantage is especially noticeable in the quantitative prediction of experimentally observed features of equilibrium and transitions in nanoconfined fluids.

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Metal-organic frameworks (MOFs) as biomolecules drug delivery systems for anticancer purposes

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Metal-organic frameworks (MOF) have been studied for infinite applications. Among these, anticancer therapy has surely attracted great interest due to the intrinsic characteristics of MOFs: large surface area, tunable porosity, remarkable biocompatibility, easy production, and the possibility to further functionalize the realized nanoparticles are the main reasons that make MOFs the ideal candidates to overcome traditional chemotherapy limits and resistance. Smart MOFs are becoming particularly relevant, as they can be activated by specific endogenous or exogenous stimuli and release their cargo only under the selected conditions. Tumor microenvironment (TME) offers the possibility to take advantage of its peculiar composition to design and build smart nanoparticles, able to selectively release the therapeutic payload only in the environment surrounding cancer cells or directly in the intracellular environment. I will discuss recent applications in anticancer MOF-based nanoparticles loaded with special focus on TME-responsive MOFs and some synthetic procedures to further underline the myriad of possibilities offered by these hybrid metal-organic structures.

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Non-Fickian effects on desorption from source rocks' organic matter

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Shale-gas recovery from unconventional reservoirs is a very slow process that exhibits "anomalous" behaviour at large scales such as non-Fickian productivity declines [1] (i.e. the recovery curves evolve at early times as t^a with a $a < 0.5$). Such non-Fickian behaviors have also been observed experimentally on methane desorption from coal samples [2]. Recent numerical studies, focusing on the microporosity of the organic matter called kerogen (where the hydrocarbons are produced and trapped during maturation), has been carried out to elucidate transport properties [3,4,5,6] using various atomistic reconstructions of kerogens' microporosity and by neglecting or not the effects of flexibility of the carbonaceous microporous structure that can lead to important swelling due to fluid adsorption. Despite those results, the underlying quasi-stationary assumption usually made to upscale the obtained transport properties imposes a Fickian desorption regime in contrast with the observations.

By using Non Equilibrium Molecular Dynamics (NEMD) we show that the kinetics of desorption from an amorphous microporous structure lead to non-Fickian effects similar to those observed on the fields and in experiments. We highlight that the general scaling t^a for the early regime of the recovery curve might not be unique as the exponent a depends on the portion of the curve we fit and that this exponent depends on the rigidity of the carbon microstructure while always remaining below 0.5 as observed. By confronting the NEMD results with a Fickian diffusion model solved numerically we show that the Fickian desorption regime ($a=0.5$) is very robust, e.g., a concentration dependent diffusion coefficient still lead

to a Fickian desorption regime. By investigating the equilibrium mechanism of diffusion we suggest a qualitative explanation of the non-Fickian effects revealed by NEMD, thus shedding light on observations made on the fields and in experiments.

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Revealing the cage-by-cage mechanism of liquid water intrusion into porous solids

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ZIF-8 has attracted major research interest as a pivotal candidate material for the storage and dissipation of mechanical energy via liquid intrusion and extrusion. However, the underlying physical mechanism by which the liquid enters the porous structure has remained the subject of rigorous scientific debate. Herein, via a joint theoretical-experimental investigation, encompassing molecular dynamics and stochastic modelling, in conjunction with in-operando synchrotron imaging of high-pressure intrusion experiments, we reveal that liquid intrusion proceeds via cascade filling of connected cages, with penetration proceeding via the formation of hydrogen bonds across neighboring cages. Cascade filling breaches a neighboring cage when a threshold intra-cage coherence is achieved, such that filling proceeds cage by cage. This understanding of a coherent wetted domain of interconnected cages is in contrast to recently proposed homogenous condensation of water vapor inside the nanoporous structure [1], and informs of the importance of pore connectivity in candidate materials for intrusion-based applications.

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Surprising effects of vacancies on surface hydrophobicity

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The conventional wisdom regarding the hydrophobicity of chemically heterogeneous surfaces is that introducing a hydrophilic site into an otherwise hydrophobic surface reduces its hydrophobicity. Consequently, increasing the number of hydrophilic sites should further decrease the hydrophobicity of the surface. In this talk, I will briefly review the results that have led to this perspective and methods for probing surface hydrophobicity in molecular simulations. Then, I will discuss our ongoing work that examines the impact of vacancies on the water-MoS₂ interface. MoS₂ is a mildly hydrophobic surface that often contains sulfur vacancies. A sulfur vacancy effectively acts as a positive charge, such that a water molecule can strongly bind to the vacancy in a similar manner to water interacting with a cation. As a result of this strong binding, a sulfur vacancy could be termed hydrophilic – it pins water to the surface. We find that introducing multiple sulfur vacancies in MoS₂ can result in non-trivial changes to surface hydrophobicity and the properties of interfacial water in general.

Time-resolved pressure-induced potential in nanoporous materials: Measurements, interpretation and some implications for understanding fluid properties in nanopores

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In water-soaked charged nanoporous materials, a number of interesting phenomena is caused by the commensurability of pore size with the Debye screening length. Many researchers have already discovered for themselves surface conductance. Streaming potential/current are less known. Still less known is the effect of surface conductance on streaming potential (SP). Taken into account properly (along with overlap of diffuse parts of electric double layers), it gives rise to maxima on the dependencies of SP on surface-charge density in nanopores. Accordingly, for a given nanopore size, electrolyte valence type, ion mobilities and concentration, there are maximum theoretically possible absolute values of SP coefficient. In experiments, essentially larger values are sometimes observed, which gives rise to speculations concerning (in)applicability of classical space-charge model. In particular, non-zero slip at pore surfaces is evoked to explain anomalously large absolute values of SP coefficient.

We will show that such values can be alternatively explained by the buildup of salt-concentration gradients and corresponding diffusion potentials. This will be illustrated by time-resolved measurements of transient filtration potential making possible extrapolation to very short times and determination of genuine streaming-potential coefficient. Additionally, salt diffusion permeability, salt reflection coefficient and ion transport numbers in nanopores can also be estimated using a relatively simple model. In contrast to SP coefficient, these other properties are monotone functions of surface-charge density, which makes possible its unambiguous determination.

We will see that for nanoporous polymer films with the pore size of around 30 nm in moderately dilute electrolyte solutions (KCl), the diffusion component of pressure-induced potential can easily exceed the genuine streaming potential by a factor of 3-4. We will also see that after some relatively short periods of time, the measured filtration potential appears to approach steady-state values. Given that measurements are often not properly designed to be time-resolved, these values can be erroneously taken for streaming potentials. Interpreted as such by using space-charge model they may give numbers far exceeding maximum possible values.

In summary, time-resolved electrokinetic measurements are indispensable and, in principle, relatively simple. One just needs to know that they are necessary.

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Understanding mass transport in reactive porous materials for advanced energy storage

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Porous materials play a crucial role in many industrial applications such as energy storage, catalysis, and separation technologies due to their high permeability, which allows for efficient mass transport. In recent years, there has been a growing interest in the application of porous materials for energy storage due to their unique characteristics, such as large surface area and high stability, particularly for Lithium-Ion Batteries (LIB) [1]. LIBs currently on the market employ a sandwich structure, where powdered anode and cathode materials and a binder are spread onto metal sheets serving as current collectors. A polymeric separator is placed between them, and everything is impregnated with the electrolyte [2]. The Pseudo Two-Dimensional (P2D) model [3] is a key tool for predicting and modelling material performance. It is an enhanced version of the traditional Newman model [4], where the three domains are homogenized, and mass transport is approximated with an effective coefficient. However, the accurate characterization of porous materials' mass transport properties, which is challenging to

measure in operando condition due to the high reactivity of the devices, remains a significant reliance for the P2D model.

In this talk, we will discuss the current state of research and understanding of mass transport in reactive porous materials for advanced energy storage. Specifically, we will show how atomistic simulation can help reveal the underlying mechanisms that govern mass transport in these materials at the atomic and molecular scale. The diffusion coefficient can be obtained for the pure material even using classic molecular dynamics (MD) simulations where the system's connectivity is fixed. However, in this case, only the direct-hopping of the ions is allowed, which can be sufficient for non-reactive system like the percolation of the Li atom in the graphite [5]. While for a more complex system, like the Solid Electrolyte Interface (SEI), which is a mixture of organic and inorganic products of electrolyte decomposition, reactive MD simulation is needed. For instance, in the LiF layer of the SEI, the ab initio methods have shown how diffusion primarily occurs through the knock-off mechanism, where an interstitial atom displaces a Li atom from its lattice site [6]. A tailored van Duin's reactive force field (ReaxFF) [7] was used to show at the atomistic scale this phenomenon. However, the resulting new parametrization shows a substantial limitation in correctly capturing the energy barrier of the diffusion process. Therefore, new and advanced Neural Network Force Field (NN-FF) [8] was implemented, showing a better agreement with the first principle calculation, and thanks to the scale-up capability of these methods, they can be used to predict transport properties in larger systems and for longer times having a better estimation of the diffusivity.

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Water and solutions in nanoporous media: Capillarity, osmosis and phase change

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I will discuss a series of experiments that illustrate the rich physics of phase transitions and transport in nanopores, using water and salt solutions. In particular, I will first show how adding solutes to water changes its thermodynamic behavior through the measurement of evaporation/condensation isotherms. I will also show that these measurements provide useful information about how nanoscale confinements modify the conditions for crystallization and deliquescence of salts. Finally, I will present results about the dynamics of water uptake and evaporation upon humidity changes, showing different behaviors depending on the applied conditions and their history. Most of these observations can be rationalized using a combination of capillarity, osmosis and nucleation.

Water confined in nanopores: What do we know about it and what is it good for?

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Water confined in pores a few nanometers in size plays a dominant role in many natural and technological processes, ranging from clay swelling, frost heave and catalysis, to colloidal stability and protein folding, to transport across artificial nanostructures and biomembranes. In nanoporous media, the geometrical confinement and pore wall-fluid interactions as well as the complex pore morphologies can significantly alter the physico-chemical equilibrium and nonequilibrium properties of water, causing e.g., molecular structuring of the fluid, huge negative Laplace pressures in the liquid and altered shear viscosities.

In the first part of my talk, I will present opto-fluidic, X-ray and neutron scattering experiments on capillarity-driven transport, self-diffusion dynamics of water and aqueous electrolytes in nanoporous solids [1, 2] as well as on the interplay of water capillarity with the elasticity of the confining solid [3, 4]. The observations on the effective porous medium scale will be related to the properties of single nanopore fluids [2], also using computer simulations. In the second part of my talk, I will illustrate that exploiting the peculiar nanofluidics of water in combination with self-organized porosity in solids offers a completely new design space for sustainable, active integrated materials with functional diversity. In particular, I will present porous materials with electrically switchable wettability and hydraulic permeability [5] as well as large electrochemical-mechanical actuation for potential applications in lab-on-a-chip fluidics, sensing, water filtration, and energy conversion [5,6,7].

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