# Transport of water in soft porous media

**Abstract**

The aim of this PhD thesis is to provide, based on experimental studies, a description of water transport in soft porous materials. Water in soft matter is indeed subjected to several interplaying effects that influence transport at the nanoscale: hydrophilicity/hydrophobicity heterogeneities of the surfaces, diffuse boundaries and deformations or mechanical effects. These situations are currently met in many systems, from polymeric membranes or wood-based materials to biological processes. Using porous polymers-based samples representative of soft porous materials, complementary experimental investigations of the atomic scale (neutron scattering) and mesoscale (NMR) will be carried on in order to provide relevant data for the validation of predictive models. Although the work will be experimental, the student will closely interact with the theoretical counterpart.

## Context and objectives

Transport of water in soft porous materials is relevant to a broad range of applications such as ultrafiltration and reverse osmosis processes, where polymeric membranes are employed in filtration/separation, or energy related processes where proton conducting media (Nafion for instance) are used. It also pertains to important fields such as those dealing with wood/cellulosic materials, food processing and is of upmost importance in many biological processes (transport through cellular membranes). In spite of its importance, transport in soft matter remains unclear in many respects, with three key points that are



*Figure 1: Deformable surface with heterogeneities in hydrophilic/hydrophobic properties and variable penetration thickness for water.*

illustrated in figure 1. ● **Surface heterogeneity.** Hydrophilicity/hydrophobicity heterogeneities of the confining surface, which are inherent/typical to soft matter, become dominant at the nanoscale and lead to complex phenomena with possible nanoseggregation, slippage, surface diffusion, etc. ● **Diffuse boundary.** The penetration depth of water at the surface of the confining matrix is ill-defined due to complex adsorption phenomena and possible permeability ("porosity") of the surface. This results in a strong coupling between water adsorption and the behavior of the membrane inner surface. ● **Deformations, mechanical effects.** Compliance effects such as swelling, which are inherent to the soft nature of the host medium, depend on the thermodynamic (T, μ, σ) state of confined water. Although they cannot be ignored in the case of soft environment, such effects are usually not taken into account when describing water transport in porous materials. A correct description of water transport in soft confinement should therefore consider adsorption and confinement effects, microscopic diffusion mechanisms, and local as well as global host deformations.
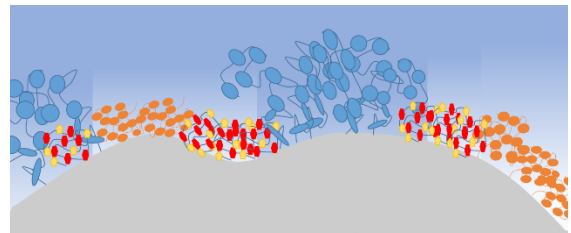
Such a goal can be reach in using a multiscale strategy from the atomic to the macroscopic dimensions. The combination of complementary experimental techniques (Neutron scattering, NMR and macroscopic permeance measurements) will enable a severe test of the proposed theoretical description based on molecular dynamics, statistical mechanics and rigorous upscaling to the macroscopic scale based on the poromechanics' formalisms to calculate the macroscopic permeance of the system $K(\mu,T,\boldsymbol{\sigma})$, *i.e.* the response of the flow rate $\upsilon$ to a pressure gradient $\boldsymbol{\nabla}\mathbf{P}$, as a function of temperature $T$, water chemical potential $\mu(P,T)$, and external stresses $\boldsymbol{\sigma}$. as proposed by Darcy's law: $\upsilon=K\boldsymbol{\nabla}\mathbf{P}$.

## Thesis project.

In this context, the proposed PhD project aims at providing an experimental characterization of water transport in soft porous materials under mechanical load at constant strain or stress (isochoric or

oedometric conditions, respectively). Combining neutron scattering and NMR measurements on the same systems and similar conditions, we will gain insights into the fundamental mechanisms while understanding how each scale affects water transport in soft porous environments. The materials considered in the current project will be purely hydrophilic, in order to better <u>address the mechanical deformation issue</u>. We will work on a well defined set of samples made of polymeric porous materials (Polymers with Intrinsic microporosity, PIM, and self-assembly of block copolymers) covering the requested range of parameters in terms of pore size (1-100 nm) and elastic moduli. The structure of the materials and the diffusion coefficient of water will be characterized in various conditions of hydraulic flow and mechanical load $\sigma$ (<1 kbar).

**Atomic scale structural and dynamics characterization**. The first part of the PhD project is to get a quantitative description of the structural variations and diffusion processes under various conditions of flow and mechanical load of the investigated samples.

The atomic scale will be mainly investigated by neutron scattering, although X-rays may be used as well for structural characterization. But thanks to the possibility of using $D_2O$ instead of $H_2O$, neutron scattering will offer much better contrast. Because of the polymeric nature of the matrices, we do not expect to obtain precise information from wide-angle diffraction and will rather look at the small Q range (SANS measurements).

QENS is then the technique of choice for the characterization of water transport at the nanoscale, enabling the analysis of relaxation processes over time and length scales that fully correspond to that of water diffusion. Information on diffusion coefficients and mechanisms such as jump length, residence time etc. will be obtained. Moreover, isotopic substitution (H/D) enables not only selective enhancement of the signal from either the host or water, but also varying the proportion of coherent and incoherent scattering, thus providing an independent determination of collective and self-diffusion processes through the determination of self and collective diffusion coefficients ($D_s$ and $D_0$, respectively). More precisely, $D_0$ will be estimated at the molecular scale using coherent neutron scattering. Quantitative analysis of the elastic incoherent contribution (EISF) will also provide the number of water molecules trapped into the walls, a precious information for understanding potential swelling effects.

**NMR**. In a second part of the project, the PhD candidate will use Nuclear Magnetic Resonance Dispersion (NMRD), Pulsed Field Gradient NMR (PFG-NMR) and 2D $T_2$-$\Delta$-$T_2$ NMR relaxometry to provide extended dynamical and structural information at the nm to the μm length scales, and from the ns to the μs timescale, complementary to QENS and neutron spin echo techniques. Information such as the average residence time on the surface, the local and macroscopic self-diffusion coefficient of water molecules in confinement or the molecular exchanges between two pores having a different size will be extracted. Moreover, the so-called tortuosity of the pore network and pore size distribution will be probed in an original way. The measurements will be performed at the PHENIX laboratory (Paris) and supervised by A.-L. Rollet, G. Mériguet and Pierre Levitz.


**Contact:**
**Marie Plazanet, LIPhy, Grenoble**
marie.plazanet@univ-grenoble-alpes.fr

**Anne-Laure Rollet, PHENIX, Paris**
anne-laure.rollet@upmc.fr

**Funding : ANR / ILL, starting at latest Oct. 2018.**