Experimental report

17/09/2018

Proposal: **6-07-34** **Council:** 4/2018

Title: Water dynamics in mesoporous with periodically alternating surface interaction

Research area: Physics

This proposal is a new proposal

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Denis MORINEAU

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Samples: Water
divinylaniline-bridge PMO $((C_2H_2)-C_6H_3NH_2-(C_2H_2))_x-(SiO_2)$
biphenyl- Bridge PMO $(C_{12}H_8)_x-(SiO_2)$

Instrument	Requested days	Allocated days	From	To
IN5	5	3	14/09/2018	17/09/2018

Abstract:

Nanoconfined and interfacial liquid water is ubiquitous in Nature and plays a central role in many applications. This explains why the dynamics of liquid water in spatially confined geometry has been extensively studied, especially using mesoporous silica as a model system. According to the abundant QENS literature, it appears that the chemical nature of the surface of nanoporous materials can be envisioned as a driving parameter of water dynamics. Our aim is to make use of this phenomenon in order to tune the interfacial mobility of nanoconfined water from a spatial modulation of the surface-water interaction. The rationale of the project relies on our capability to design nanochannels that exhibit a periodic successions of hydrophobic and (weakly or highly) hydrophilic units, which are perfectly localised along the main pore axis at the molecular scale.

Water dynamics in mesopores with periodically alternating surface interaction

Version 17 Sept. 2019

This is a preliminary report of the experiment (#6-07-34) performed on IN5, 14-16 Sept. 2018.

Context: Mesoporous silica has been extensively used as a model system to study the dynamics of liquid water in confined geometry. This field has greatly benefited from a continuous better control of the conditions of confinement starting from disordered porous Vycor [Bellissent-Funel 1995], to mesostructured silicas such as MCM-41 and SBA-15 [Faraone 2003, Takahara 2005], and eventually hydrophobically modified MCM-41 [Faraone 2009], or Zr−OH and Al−OH terminated MCM-41 surfaces to immobilize water molecules [Briman 2012].

General aim of the project: The chemical nature of the surface of nanoporous materials can be envisioned as a driving parameter of water dynamics. Our aim is to tune the interfacial mobility of nanoconfined water from a spatial modulation of the surface-water interaction. The rationale of the project relies on our capability to design nanochannels that exhibit a periodic succession of hydrophobic and (weakly or highly) hydrophilic units, which are perfectly localised along the main pore axis at the molecular scale.

Biphenyl- (BP) and divinylaniline- (A) bridged Periodic mesoporous organosilicas (PMOs) materials were be used as prototypes of hydrophobic and hydrophilic units, respectively (cf. Figure 1). These PMOs exhibit a molecular-scale periodicity (1.1nm) along the pore axis. Hence, the surface polarity of the pore walls is modulated between hydrophobic/hydrophilic (organic) and hydrophilic (silicate) layers.

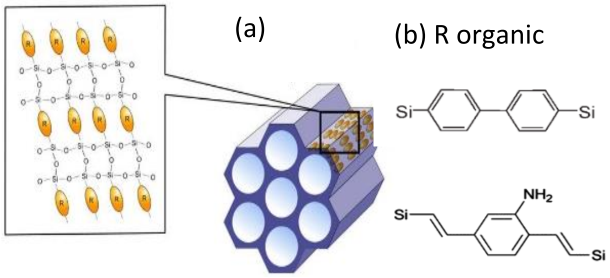

Figure 1. (a) Crystal-like arrangement of alternating silica and bridging organic units R in mesoporous PMO. (b) Organic bridging organic units with different hydrophobicity (after Hoffmann et al. 2006).

Objective and implementation of the experiment (#6-07-34):

The objective of this experiment was to assess the dynamics of water at different temperatures and at a complete filling of the porosity. We successfully measured the incoherent quasielastic scattering intensity of water confined in ***two PMOs (BP-PMO and A-PMO) at 4 different temperatures (from 300K to 240K)*** encompassing regions from the normal to the supercooled liquid states. We also made a rapid measurement on ***bulk water for comparison***. Standards (empty cell and Vanadium) were also measured. The incoherent quasielastic scattering intensity was acquired with an incoming wavelength of 8A, in order to achieve a very good energy resolution, balanced by the necessity to maintain a reasonable flux given the small amount of material in the beam (90 to 20 mg of water, depending on the porosity). Under these conditions, a satisfying statistics was achieved with a count period of 3-5 h/spectrum.

The intended experimental program was shortened because of the failure of one chopper after 48h of experiment. It induced ***one day of backlog*** and ***pending experiments on water confined in bare silica and on the empty A-PMO***.

Sample preparation : The samples were prepared one week in advanced at Rennes, by equilibrating the dried porous powders contained in the IN5 flat aluminium cells in a desiccator for 2 days. The partial pressure of the water vapour in the chamber (RH=82%) was controlled with a saturated solution. Then the cells were sealed with an indium joint and sent as-is to the ILL. Companion samples were prepared in parallel in the same conditions in DSC pans in order to check to filling procedure by calorimetry. The thermograms measured just before QENS experiments confirmed the complete filling of the porosity without excess water, which is also in agreement with gravimetric measurements (cf. Fig. 2).

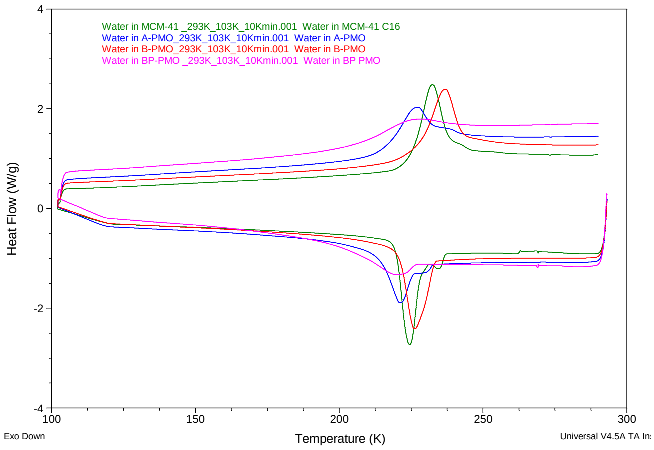

Figure 2. DSC thermogram of the samples filled at RH=82% in parallel with the one measured on IN5. The depressed melting point at about 238K, confirms the complete filling of the porosity without excess water.

Dynamic structure factor: The data reduction was performed using standard procedure under LAMP. It includes transformation from time of flight to energy, normalization to Vanadium, correction from detector efficiency, background and transformation from scattering angles to a regular list of wavevector. The incoherent scattering structure factor of water confined in BP-PMO is shown in Fig. 3 at a constant Q (1.0 A-1) for the 4 studied temperatures. The resolution is also presented for comparison.

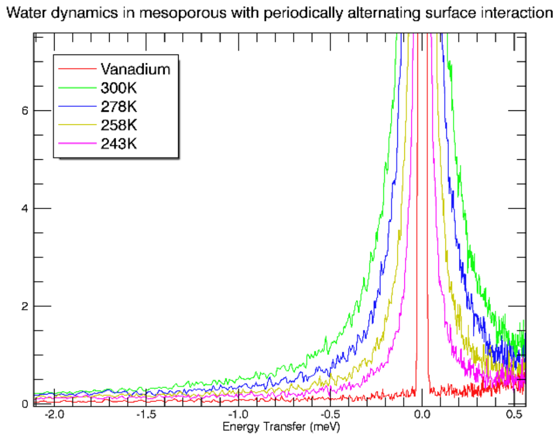

Figure 3. S(Q,W) of water confined in BP-PMO as a function of temperature for Q=1.0A^{-1}.

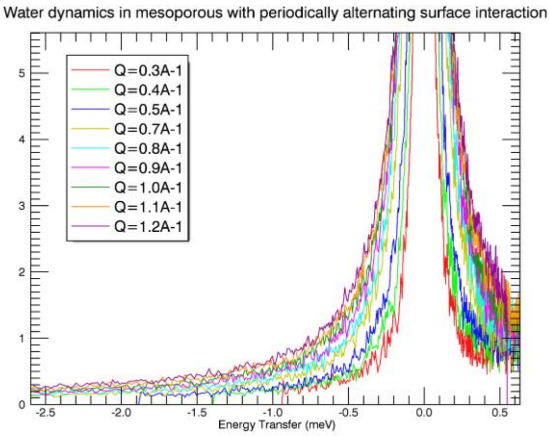

Figure 4. S(Q,W) of water confined in BP-PMO as a function of Q for T=300K.

It presents a distinct quasielastic broadening, which extends well above the elastic resolution of IN5. The quasielastic signal obviously sharpens on cooling. Figure 4 shows the Q-dependence of the quasielastic line as a given temperature. A clear broadening is observed when the value of the transfer of momentum increases. The dynamic structure factor measured for water confined in A-PMO (not-shown) follows the same qualitative trend, albeit difference from the quantitative point of view.

Preliminary QENS fits

We have performed preliminary fits of the data using standard models on LAMPS. For confined water, both in A-PMO and BP-PMO, the incoherent dynamic structure factor could be simply fitted by the sum of a single Lorentzian and a Dirac function.

The *Q*-dependence of the elastic broadening reveals that a fraction of mobile molecules exhibit jump-diffusive dynamics with a reduced mobility with respect to the bulk (cf. Fig. 5). The Q-dependence of the additional elastic component (absent for bulk) indicates that molecules involved in this diffusive process are hindered at large distances.

This phenomenon could be described by fitting the EISF with a model of diffusion in a sphere (cf. Fig. 6). It also indicates that the radius of the sphere continuously decreases on cooling. Moreover, the fraction of non-mobile molecules (within the resolution of IN5 @8A), also continuously increases on cooling, being up to 75% in the deeply supercooled region (243K).

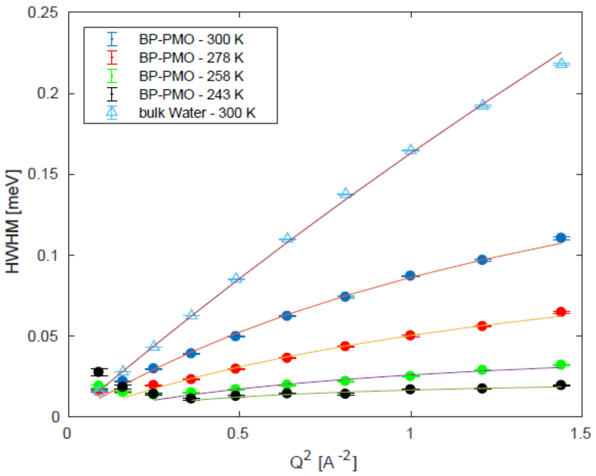

Figure 5. Width (HWHM) of the quasielastic line fitted by a Lorentzian function for bulk Water at 300K (upper curve) and Water confined in BP-PMO at four different temperatures. Lines are best fits of a jump diffusion model.

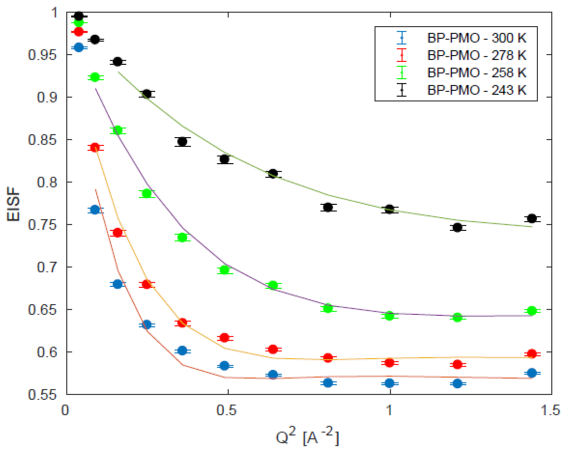

Figure 6. Relative intensity of the elastic component (EISF) for Water confined in BP-PMO at four different temperatures. Lines are best fits of diffusion in a rigid spherical cavity with a fraction of non-mobile molecules.

<u>References by the applicant:</u>

[Hoffmann 2011] **Chem.Soc.Rev.,** (2011), 40, 608-620.
[Mietner 2017] **Angew. Chem. Int. Ed**. (2017), 56, 12348 –12351
[Mietner 2018] Mietner et al. **J. Phys. Chem. C** (2018), 122, 12673−12680

<u>Other references:</u>

[Bellissent-Funel 1995] **Phys. Rev. E** 51 (1995) 4558. [
Faraone 2003] **J. Chem. Phys.** (2003), 119, 3963.
[Takahara 2005] **J. Phys. Chem**. B (2005), 109, 11231-11239
[Mamontov 2006] **J. Chem. Phys.** 124, 194703 (2006);
[Faraone 2009] **J. Chem. Phys.** (2009) 130, 134512
[Briman 2012] **J. Phys. Chem. C** (2012), 116, 7021−7028
[Kiwilsza 2015] **J. Phys. Chem. C** (2015), 119, 16578−16586
[Osti 2016] **Chem. Phys.** (2016) 465–466 1–8