Experimental report

19/03/2021

Proposal:	**6-07-45**	**Council:**	10/2018
Title:	Water dynamics in mesoporous with periodically alternating surface interaction		
Research area:	Physics		

This proposal is a continuation of 6-07-34

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Samples: Water
biphenyl- Bridge PMO (C12H8)x-(SiO2)
divinylaniline-bridge PMO ((C2H2)-

Instrument	Requested days	Allocated days	From	To
IN5	4	1	28/06/2019	01/07/2019
IN16B	4	3	13/09/2019	16/09/2019

Abstract:

Liquid water in confined geometry has been extensively studied, and its dynamics is largely determined by the chemical nature of the confining nanoporous materials.
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.
In a previous experiment (6-07-34, IN5, 14-17 Sept. 2018), we have initiated a project at ILL on the dynamics of liquid water confined in Periodic Mesoporous Organosilicas (PMOs). 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 pore at the molecular scale.
Albeit the unforeseen stop of the experiment after 48 hours (due to a chopper failure) and the short delay between the experiment completion and the deadline for proposal application, we could conduct a complete reduction of the data and preliminary fits of the results. We formulated first conclusions about the water dynamics in PMOs, which underline the prime interest to extend our study towards longer timescale and partially filled samples.

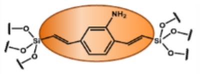
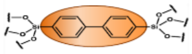
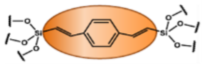
Water dynamics in mesopores with periodically alternating surface interaction

Summary: We have investigated the dynamics of liquid water confined in mesostructured porous silica (MCM-41) and periodic mesoporous organosilicas (PMOs) by incoherent quasielastic neutron scattering experiments. The effect of tuning the water/surface interaction from hydrophilic to more hydrophobic on the water mobility, while keeping the pore size in the range 3.5-4.1 nm, was assessed from the comparative study of three PMOs comprising different organic bridging units and the purely siliceous MCM-41 case. An extended dynamical range was achieved by combining time-of-flight (IN5B) and backscattering (IN16B) quasielastic neutron spectrometers providing complementary energy resolutions. Liquid water was studied at regularly spaced temperatures ranging from 300 K to 243 K. In all systems, the molecular dynamics could be described consistently by the combination of two independent motions resulting from fast local motion around the average molecule position and the confined translational jump diffusion of its center of mass. All the molecules performed local relaxations, whereas the translational motion of a fraction of molecules was frozen on the experimental timescale. This study provides a comprehensive microscopic view on the dynamics of liquid water confined in mesopores, with distinct surface chemistries, in terms of non-mobile/mobile fraction, self-diffusion coefficient, residence time, confining radius, local relaxation time, and their temperature dependence. Importantly, it demonstrates that the strength of the water/surface interaction determines the long-time tail of the dynamics, which we attributed to the translational diffusion of interfacial molecules, while the water dynamics in the pore center is barely affected by the interface hydrophilicity.

The results from this experiment were published in **A. Jani et al*., J. Chem .Phys.* (2021), 154, pp.094505. ⟨10.1063/5.0040705⟩**

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. To reach this goal, we used a purely siliceous MCM-41 matrix and three PMO materials with different bridging groups: biphenyl BP-PMO, divinylbenzene DVB-PMO and divinylaniline DVA-PMO. The structural parameters of all the matrices are summarized in Table 1.

Name	Bridging unit name	Bridging unit	Repetition distance of the bridging unit along the pore axis (nm) [a]	Pore volume ($cm^3.g^{-1}$) [b]	Specific Surface Area ($m^2.g^{-1}$) [b]	Mean pore diameter (nm) [b]	Hydrophilicity [c]
MCM-41	**-**	**-**	**-**	**0.893**	**1077**	**3.65**	**High**
DVA-PMO	**Divinyl-aniline**		**1.18**	**0.890**	**1223**	**3.5**	**High**
BP-PMO	**Biphenyl**		**1.196**	**0.445**	**786**	**3.5**	**Low**
DVB-PMO	**Divinyl-benzene**		**1.18**	**0.990**	**864**	**4.1**	**Low**

QENS experiments and data analysis:

IN5B (28/06/2019-01/07/2019) The disc chopper time-of-flight spectrometer IN5B was used with an incident wavelength of 8 Å. In this configuration, the resulting energy resolution ΔE around the elastic peak is about 22 µeV (FWHM), corresponding to a timescale ($t=\Delta E/\hbar$) of about 30 ps. The quasielastic signal retained for the data evaluation covered an energy range ($E=\hbar\omega$) between -5.0 and 0.7 meV and a Q range between 0.2 and 1.3 $Å^{-1}$.

IN16B (13/09/2019-16/09/2019) The high-resolution IN16B spectrometer was chosen with unpolished Si (111) monochromator and analyzers in backscattering geometry, which corresponds to an incident wavelength of 6.271 Å and results in an energy resolution of 0.75 µeV and a corresponding timescale of about 1 ns. The energy range was ±30 µeV with a Q range between 0.19 and 1.83 $Å^{-1}$. The background chopper of the instrument was run in its high signal-to-noise mode. A cryofurnace and an ILL orange cryostat, were used on IN16B and IN5B spectrometers in order to regulate the sample temperature. The measurements were performed after thermal equilibration at regularly spaced temperatures, which were reached sequentially on cooling (300, 278, 258 and 243 K on IN5B, and 278, 258 and 243 K on IN16B) with dried and water filled samples. The four different matrices were studied on IN5B, and three of them on IN16B (MCM-41, DVB-PMO, and DVA-PMO).

Data analysis: Standard data corrections were applied using the packages MANTID and LAMP provided at the ILL. The experimental intensity was corrected for detector efficiency, for the background contribution arising from the empty cell and spectrometer, and transformed into the Q and energy dependent scattering function $S(Q,\omega)$. The fitting of scattering functions $S(Q,\omega)$ in the frequency domain was carried out using the QENSH program provided by the Laboratoire Léon Brillouin (LLB, Saclay, France).

Results

The QENS spectra of water filled DVB-PMO and MCM-41 are shown in Fig. 1. Qualitatively similar results were obtained for water confined in the other matrices

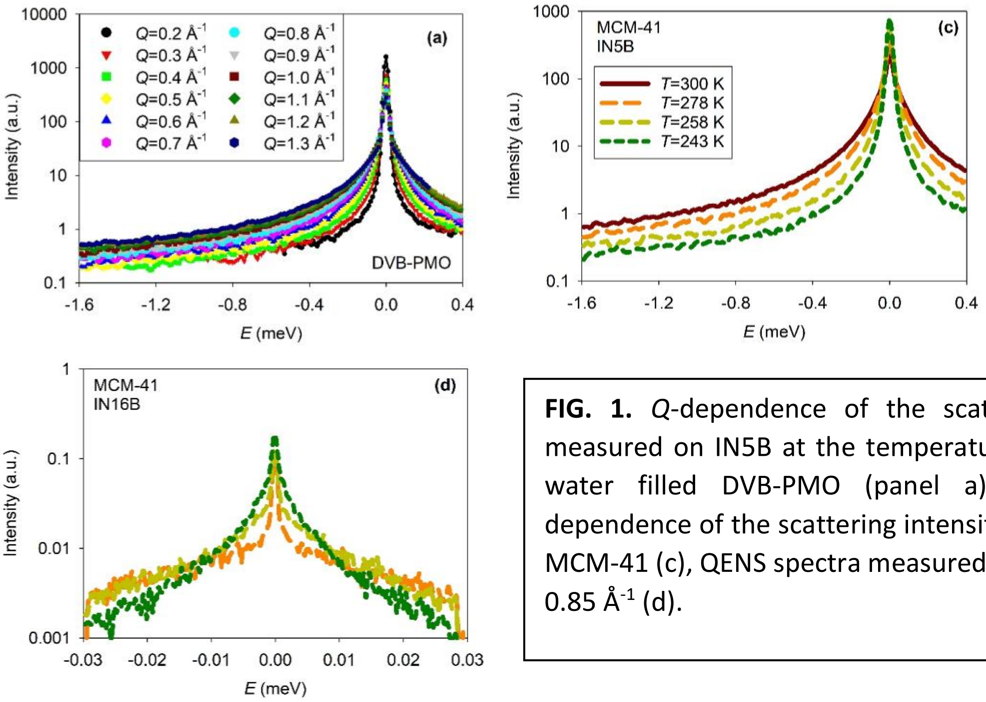


FIG. 1. *Q*-dependence of the scattering intensity measured on IN5B at the temperature *T* = 278 K of water filled DVB-PMO (panel a) ; Temperature dependence of the scattering intensity of water filled MCM-41 (c), QENS spectra measured on IN16B at *Q* = 0.85 Å^{-1} (d).

The QENS spectra were successfully fitted by QENS models indicating the presence of two distinct dynamics, as illustrated in the case of one typical sample (cf. Fig. 2). The obtained EISFs were consistent with a local 'intra-bassin' fast dynamics (Fig. 3a) and a slower confined jump-diffusion process (Fig. 2b). The later description was also in agreement with the Q-dependence of the quasielatic width (Fig. 2c).

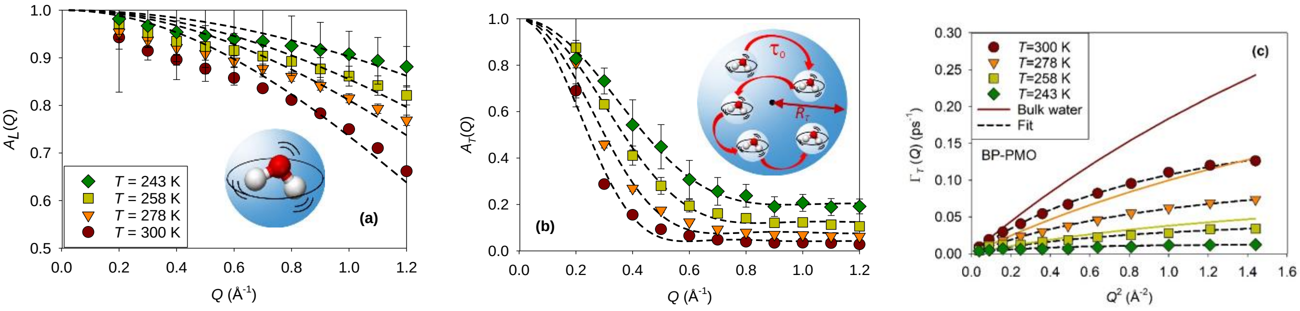


FIG. 2. EISFs of the two dynamics (a) and (b) and evolutions of the half width at half-maximum Γ_T of the sharpest Lorentzian as a function

The combination of both spectrometers provided a thorough description of the water dynamics, as a function of the temperature in terms of mobile fraction of water molecules, translation diffusion coefficient D_T, and residence time τ_0 of the mobile fraction of water molecules derived from the jump diffusion model.

For a detailed discussion of the results and conclusions about the influence of confinement and pore surface chemistry, we refer to the article **Jani et al.*, J. Chem .Phys.* (2021), 154, pp.094505. ⟨10.1063/5.0040705⟩.**