Experimental report

16/09/2019

Proposal:	**9-11-1864**	**Council:**	4/2018
Title:	Investigation of supercooled waterdynamics by confinement in dense microgel suspensions		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples: n-[C6H11NO + 0.051 C7D10N2O2] in H2O

Instrument	Requested days	Allocated days	From	To
IN16B	5	5	30/09/2018	05/10/2018
IN5	5	5	04/10/2018	09/10/2018

Abstract:

A way to avoid water crystallization and to access the so-called no man's land is to confine water in complex environments. We recently discovered that dense colloidal microgels act as efficient confining media, which are able to prevent water crystallization at any temperature. In previous neutron scattering experiments of microgels in D2O combined with molecular dynamics simulations, we detected the occurrence of a dynamical transition in the mobility of polymers, analogous to that observed in proteins, at a temperature T~250K. Simulations further showed that there is a strong coupling between polymer and water degrees of freedom. Indeed, water diffusion constant undergoes a clear discontinuity at the same temperature. We now propose to extend the neutron scattering investigations to water by studying deuterated microgels in H2O, aiming to verify the existence of the dynamical transition in water and to further explore water dynamics in the deeply supercooled regime.

The aim of the experiment was to directly measure the diffusive and relaxational dynamics of PNIPAM hydration water and investigate its behaviour across the recently observed protein-like dynamical transition at T_c = 250 K [1,2].

Measurements were carried out at IN16B and IN5 on two set of PNIPAM based samples:

- hydrogenated PNIPAM linear chains suspensions in D_2O at different PNIPAM weight concentration, to focus on the polymer dynamics.
- deuterated PNIPAM microgels suspensions in H_2O at different PNIPAM weight concentration, to highlight the dynamic contribution of the water with respect to the gelator network.

a) IN16B

We used the Si (111) monochromator with standard energy resolution. Measurements were carried out in three different configuration:

- elastic fixed window scan (EFWS), acquisition time 30 s;
- inelastic fixed window scan (IFWS) at E = 2 μeV, acquisition time 2 min;
- quasielastic scan (QENS), spectra from -30 to 30 μeV with acquisition time 1 h;

EFWS and IFWS measurements were acquired during a continuous temperature ramp from 150 K to 290 K (rate 1 K/3 min) and then while cooling the sample to 150 K (same T step). QENS measurements were done on selected samples at selected temperature. Samples and relative investigated temperature ranges are reported in Table 1.

	measurement	*T*
D-PNIPAM microgel 45%	EFWS - IFWS	150 K – 290 K
	EFWS - IFWS	290 K – 150 K
	QENS	190 K – 285 K
D-PNIPAM microgel 50%	EFWS - IFWS	150 K – 290 K
	EFWS - IFWS	290 K – 150 K
D-PNIPAM microgel 60%	EFWS - IFWS	150 K – 290 K
	EFWS - IFWS	290 K – 150 K
	QENS	190 K – 285 K
H-PNIPAM linear chain 50%	EFWS - IFWS	150 K – 290 K
	EFWS - IFWS	290 K – 150 K
H-PNIPAM linear chain 60%	EFWS - IFWS	150 K – 290 K
	EFWS - IFWS	290 K – 150 K

Table 1. Samples measured at IN16B during Exp. 09-11-1864.

In order to normalize the data, EFWS, IFWS and QENS spectra were acquired at about 4 K. Moreover, vanadium standard, the empty cell, and the signal from the empty cryostat were also measured. The measurements of the H-PNIPAM linear chain were planned but not acquired due to a PST chopper failure.

Typical QENS spectra are reported in Fig. 1. EFWS and IFWS data show a plenty of information. In general, results confirm the presence of the protein-like dynamical transition even in linear chains, thus without the structure of the microgel, supporting the role of the complex macromolecular architecture with respect to specific structural arrangements [1]. Measurements on deuterated samples and their comparison with hydrogenated ones confirm the driving role of water [2]. Finally, the outstanding *T*-resolution of IN16 data add new details to the picture of the dynamical transition. Data analysis is still ongoing.

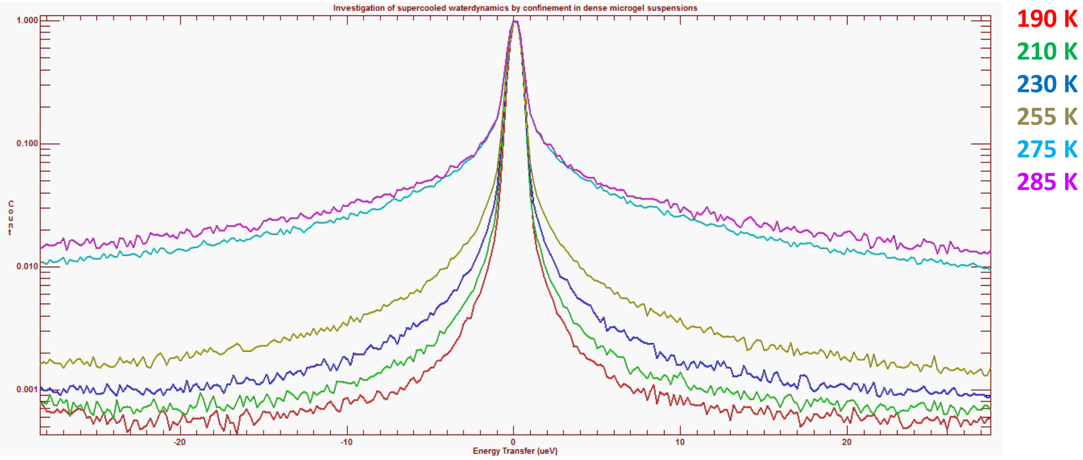

Figure 1. Temperature evolution of the experimental *I*(*Q*,ω) integrated over *Q* measured in the deuterated PNIPAM 60% microgel. Spectra are normalized to the elastic peak.

b) IN5

Measurements were carried out at low temperature, from 190 K to 288 K and then across the volume phase transition temperature T_{VPT} = 305. Samples and relative investigated temperature ranges are reported in Table 2. In addition a pure H_2O sample was also measured.

	T range	λ (Å)
D-PNIPAM microgel 45%	190 K – 320 K	5
	190 K – 288 K	8.5
D-PNIPAM microgel 60%	190 K – 320 K	5
	190 K – 288 K	8.5
D-PNIPAM microgel dry	280 K – 288 K	5
	280 K – 288 K	8.5
H-PNIPAM linear chain 60%	190 K – 311 K	5
H_2O	190 K – 287 K	5

Table 2. Samples measured at IN5 during Exp. 09-11-1864.

The samples were loaded in Al slab cells and sealed with a In o-ring. The thickness of each cell was fixed to get a transmission of about 90%. Temperature was controlled using a standard liquid nitrogen cryostat. The instrument was set to obtain an incident wavelength of 5 Å with a resolution of 96 μeV (FWHM, measured on a V sample). Some measurements were done using neutrons with incident wavelength of 8.5 Å with a resolution of 96 μeV (FWHM, measured on a V sample). Spectra were acquired after a thermalization of about 30’ for each temperature. The integration time was about 1 h (@5 Å) and 3.3 h (@8.5 Å) providing data with an excellent signal-to-noise ratio. A vanadium standard, the empty cell, and the signal from the empty cryostat were also measured.

Fig. 2 show the experimental spectra measured on the D-PNIPAM 60% at Q = 0.7 A^{-1}. Increasing the temperature up to 304 K the quasi-elastic broaden and, above that T value, spectra become smaller. This is a signature of the occurrence of the VPT.

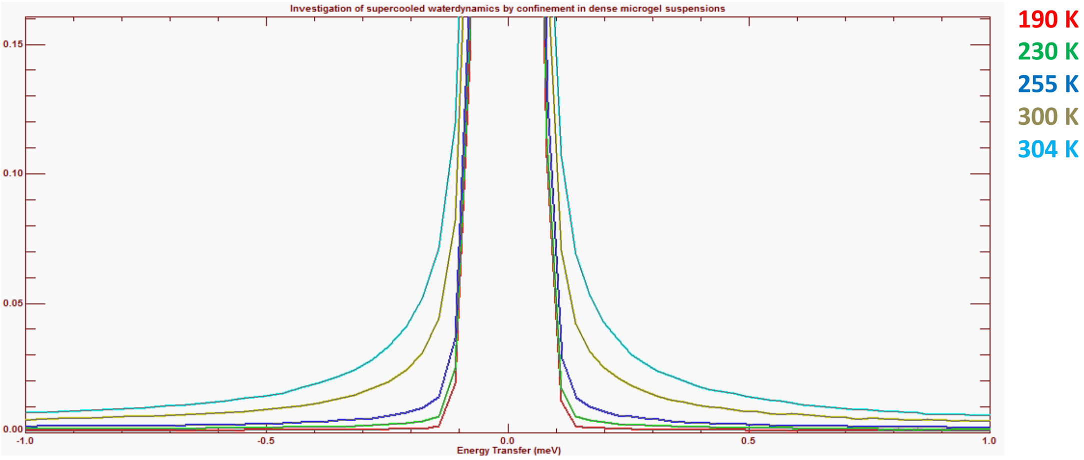

Figure 2. Temperature evolution of the experimental $I(Q,\omega)$ measured at 5 Å in a D-PNIPAM 60% microgel sample. Spectra are for Q = 0.7 A^{-1} and they are normalized to the elastic peak.

A careful analysis of results from present data can provide detailed insights on the specific nature of the microscopic motions involved in the dynamics of PNIPAM microgels and on the specific role of water in the protein-like dynamical transition [1,2].

References

[1] M. Zanatta *et al.*, Sci. Adv. **4**, eaat5895 (2018).
[2] L. Tavagnacco *et al.*, J. Phys. Chem. Lett. **10**, 870-876 (2019).