ESRF	**Experiment title:** Hydrate nucleation of a hydrophobic solute: looking for the characteristic length-scale of a critical nucleus.	**Experiment number**: HD-376
Beamline: ID2	**Date of experiment**: from: 4/12/2009 to: 7/12/2009	**Date of report**: 28/2/2011 *Received at ESRF:*
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Report:

We report here on a sucessful experiment aimed at observing the formation and growth of the methane clathrate hydrate in liquid water.

Gas hydrates have drawn great attention due to their importance on energy resources, environment, flow assurance, and geological disaster prevention. Hydrate nucleation is one of the unsolved questions in the hydrate reasearch field. Two main hypotheses are currently debated in the literature. The labile cluster model, where the water molecules arrange themselves around the dissolved apolar guest molecule in a "pre-hydrate" structure, as a result of hydrophobic interactions. The alternative model, known as the local structuring hypothesis, implies a collective cooperation between water and guest molecules, occurring on a lengthscale much larger than the individual hydrate cavity.

In order to evaluate the interplay between these opposing models, or, at best, to measure the length scale of the critical nucleus able to trigger the nucleation and growth phenomenon, we performed a small angle x-ray scattering (SAXS) experiment on the ID2 beamline.

To achieve the required thermodynamic conditions where clathrate are at equilibrium (pressure larger than 19 MPa and temperature smaller than 280 K), we made use of a high pressure cell originally developed for x-ray absorption spectroscopy measurements in transmission mode. Low-Z, plastic windows were chosen to hold the internal pressure and to be transparent to x-rays. The sample thickness was 6 mm. A mixing-circulating-pressurizing device was used to load the cell and to increase the gas pressure at the required values. In Fig. 1 we show the experimental set-up: the cell is well visible before the vacuum conical pipe to the detector, together with the high pressure line for water and gas, and the copper serpentine for cooling the ensamble. The beamline was operating in 16-bunch mode, at 16 keV.

Detector-to-sample distance was 0.89 m for a first set of measurement, providing acces to q exchanged momentum inteval within 0.1 to 8 nm^{-1}. In a second set of measurements, the detector was pushed back to 3 m from the sample for accessing smaller q's.
The cell was loaded with doubly distilled and degassed pure water at ambient pressure, then high purity methane was pressurized onto water up to 15 MPa in a first experiment, and up to 19 MPa in a second try. Once the cell loaded, we acquired 1 s counting time SAXS patterns continuously, while the temperature was cooled down to 278 K and kept constant until the crystallization is achieved. In Fig. 2 we report a typical thermal history (lower panel) for a sample at 19 MPa, together with the total absorption of the cell+sample system during time (upper panel). The discontinuous changes in the absorpion mimic the effect of the gas dissolving into water and the formation of clathrate hydrate. Raw bidimensional detector images are reported in Fig. 3 for selected time elapses (see corresponding colored points shown in Fig. 2). The Bragg ring corresponding to the 110 peak of the clathrate cubic structure *sI* appears after 3.5 hours from the onset of the isotherm. In Fig. 4 the integrated SAXS patterns corresponding to the images in Fig. 3 are reported. The changes in the slopes of the various curves occurring well before the onset of the crystallization are markers of the relevant correlation lengths that take place in the gas-water mixture.
We are confident a more quantitative analysis willl reveal the details of the nucleation mechanism that take place when the methane clathtrate hydrate are formed. A further confirmation of the observed phenomenon may be obtained by observing a different system, possibly with a higher scattering contrast with respect to water molecules.

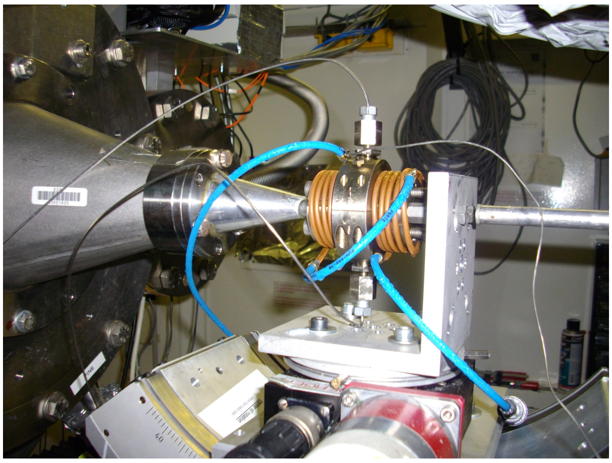

Fig. 1: Experimental apparatus.

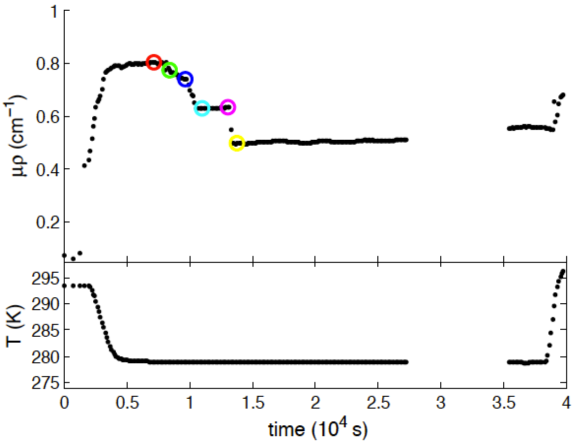

Fig. 2: Themal history and absorption profile

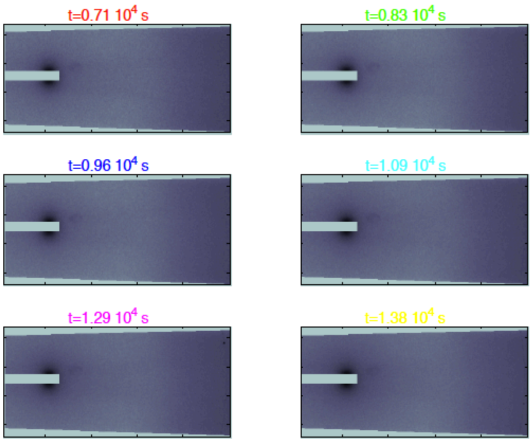

Fig. 3: Raw SAXS images at dufferent time.

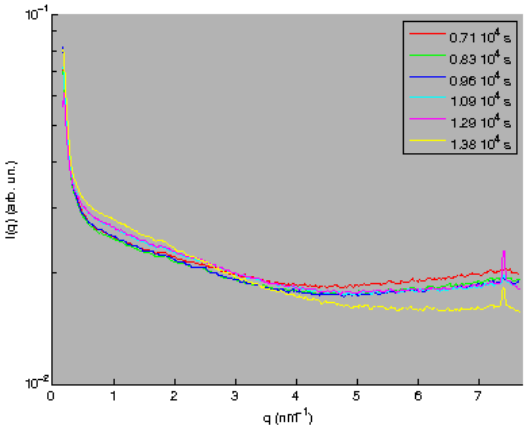

Fig. 4: Integrated SAXS patterns.