Report for experimental run SI1611 (16/07/2008 to 22/07/2008)
Main proposer: F. Venturini
Co-proposers: W. F. Kuhs, V. Honkimaki, H. Reichert, H. Schober

The aim of this experiment has been to investigate the *in situ* interfacial formation of methane hydrate films by means of high energy X-ray reflectivity measurements. In particular, to clarify the role that both pressure and temperature play during the very early stages of methane hydrate formation, a custom-designed pressure cell has been installed on the liquid surface reflectometer in use at the ID15A high energy beamline.

<u>**Experimental details**</u>

The pressure cell is shown in Figure 1. The sample, approximately 10 ml of H_2O followed by gaseous CH_4 under pressure, is loaded from the top of the chamber into the cavity of an Al_2O_3 cylinder, chosen both for its hardness and its single crystalline nature that allows minimizing the signal scattered from the window itself. Although not essential, the transparency of the window to the naked eye is also a clear experimental bonus. The sapphire window is compressed on opposite sides by two thick stainless steel plates. The internal diameter of the window is chosen to be large, i.e. 50 mm, in order to minimize the meniscus of the water. In order to hold hydrate formation pressures up to 100bar, the wall of the window is 5mm thick, giving a transmission of approximately 40% for 70 KeV X-rays. The temperature of the gas/liquid interface is carefully controlled by circulating a cooling liquid in the Cu pipes that are spiralled around the bottom and top plates.
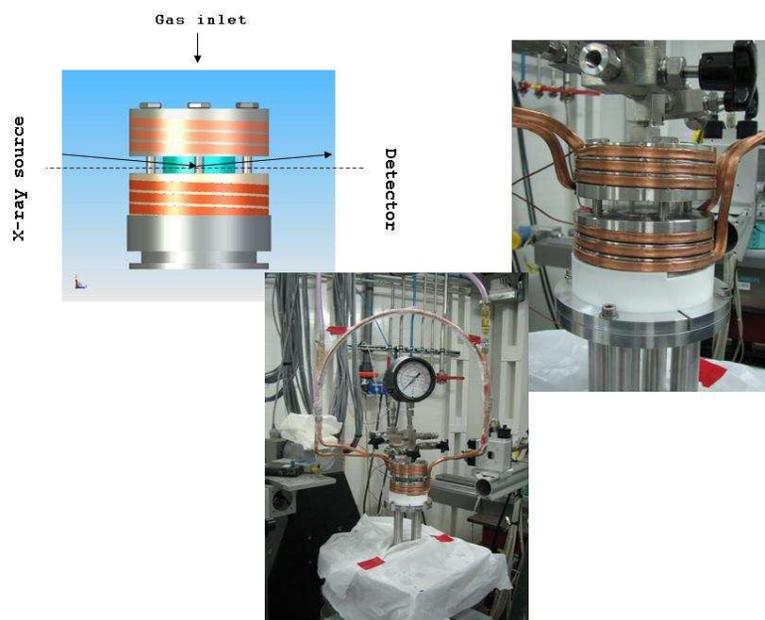
Figure 1. Top left: schematic representation of the pressure cell. The Al_2O_3 window is shown in light blue. The Cu cooling tubes are shown in orange. Top right and bottom: photos of the cell installed at the beamline.

An initial commissioning of the cell has clearly shown that, if no temperature gradient is induced between the plates, a very unstable gas/liquid interface is obtained as a result of water droplets condensing on the inside surface of the cold upper stainless steel plate. Therefore, two different cooling liquids, namely glycol and water for the bottom and top plate respectively, have been used and kept at different temperatures. Two Pt100 sensors, positioned as close as possible to the sample, measure the temperature of the respective plates. In particular, an *in situ* temperature calibration, performed by gradually decreasing the temperature of the cell until the water interface was visibly frozen, has shown that, if a temperature gradient of 15^0C is kept between the two liquids, the real temperature of the water interface is given by $T_{interface}=T_{bottom\ plate} + 2$. This initial temperature calibration has guaranteed an accurate temperature control of the gas/liquid interface throughout the experimental run.

Results

The gas/liquid interface has been investigated as a function of two of the main parameters that are known to influence the hydrate formation process, namely pressure and system subcooling, defined as $\Delta T=T_{eq}-T$, where T_{eq} is the equilibrium hydrate formation temperature at a given pressure. However, it is well known that "whiskery" interfacial hydrate films, not suitable for reflectivity measurements, rapidly cover the gas/liquid interface if the subcooling of the system is too large. The relatively wide temperature range that is accessible with our cell, typically from 0 to 30^0C, has ensured relatively small subcoolings even for the highest applied pressures.

A first set of measurements was taken, for a given pressure, as a function of the interface's temperature, hence of its subcooling. In particular, two different pressures were extensively investigated, namely 90 and 95bar. The investigated (P, ΔT) points are listed in Table 1 and shown as belonging to the horizontal lines plotted in Figure 2. They all belong to the methane hydrate stability region.

	$\Delta T(^0C)$												
P=90bar						5.7	6.1	6.6	7	7.7	8.2	8.7	
P=95bar	3.3	3.8	4.3	4.8	5.2								
P=100bar													9.9

Table 1. Temperature dependent study: measured (P, ΔT) points.

After an initial measurement taken at P=95bar and $\Delta T=3.3^0C$ the temperature of the system was gradually decreased in approximately 0.5^0C steps. For each value of ΔT at least eight successive reflectivity curves were measured, in order to investigate the time dependence of the recorded signal. After approximately 12 hours the pressure in the cell had decreased to P=90 bar and a similar procedure was followed for this value of P, with ΔT ranging from 5.7 to 8.7^0C. For P=100bar only one subcooling value was investigated, namely $\Delta T=9.9^0C$. The high-Q part of the reflectivity curves measured for P=95bar is shown in Figure 3. No detectable change is observed as a function of the system's subcooling. Furthermore, for a given set of P and ΔT no time dependence of the signal reflected from the interface is observed.
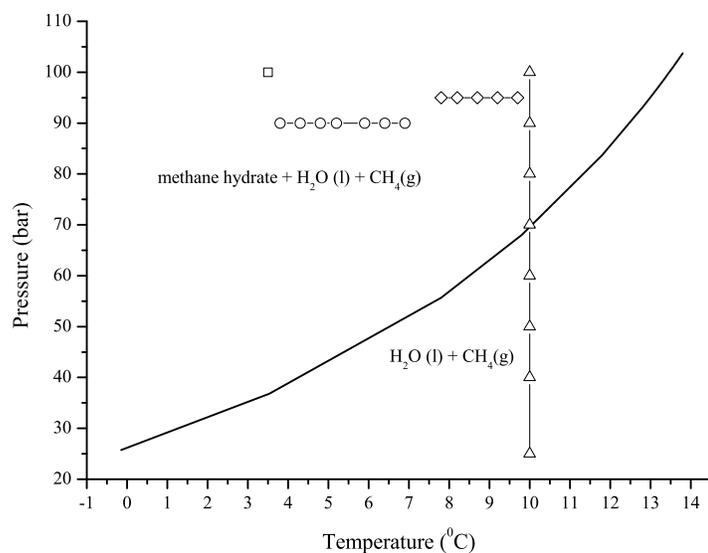
Figure 2. Portion of the methane hydrate phase diagram. The solid line represents the phase boundary. The measured (P, T) points are plotted as circles and diamonds for the two temperature dependent measurements taken at 90 and 95 bar respectively. The square represents the location of the measurement taken at P=100bar for $\Delta T=9.9^0C$. The triangles represent the (P, T) points measured, for $T=10^0C$, as a function of increasing pressure.
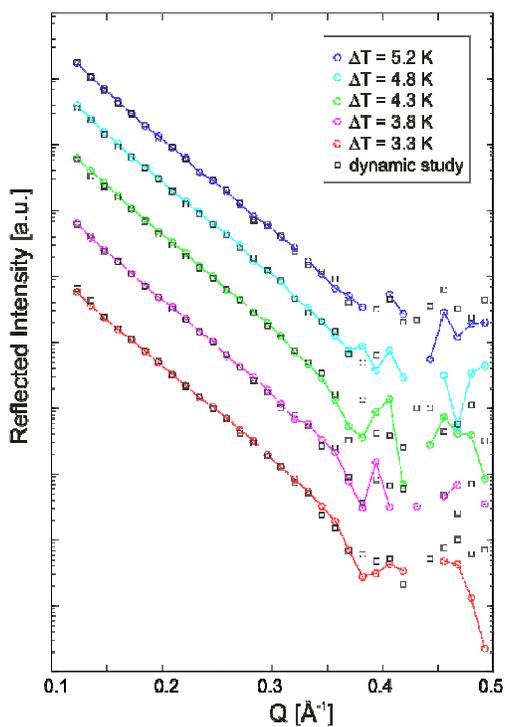
Figure 3. Temperature dependent study. All data are taken at P=95bar. The curves are shifted vertically for clarity. The subcooling of the system increases from bottom to top. For each value of ΔT, the equivalent time dependent signal is plotted in black squares.

A second set of measurements was taken, for T=10^{0}C, as a function of increasing pressure. Upon observation of Figure 2, where the investigated (P, T) points are shown as open triangles, it is clear that, within the stability region, an isothermal pressure increase is accompanied by an increase of the system's subcooling. The investigated (P, ΔT) points are listed in Table 2.

	P=25bar	P=40bar	P=50bar	P=60bar	P=70bar	P=80bar	P=90bar	P=100bar
ΔT(^{0}C)	outside stability region	outside stability region	outside stability region	outside stability region	0.32	1.67	2.82	3.8

Table 2. Pressure dependent study: measured (P, ΔT) points.

For T=10^{0}C, the initial four pressures listed in Table 2, namely 25, 40, 50 and 60 bar, place the system outside the methane hydrate stability region. The phase boundary is crossed at approximately P=70 bar. Figure 4 shows the reflectivity curves measured as a function of increasing pressure. As for Figure 3, our attention should mostly be given to the high-Q part of these curves, as the presence of the water meniscus at the interface renders the data somewhat unreliable for very small incident angles. For Q>0.1Å^{-1}, changes in the density profile of the interface when approaching the hydrate stability region clearly take place. In particular, when crossing the phase boundary, a discontinuity in the variation of the slope of the reflectivity curves is observed. At pressures higher than the hydrate formation pressure no further changes occur and the interface appears to stabilise. However, upon further examination of the high-Q part of these curves, shown in Figure 5, a layer is seen to appear for 0.37Å^{-1}<Q<0.55Å^{-1} and ΔT ranging from 0.3 to 3.3^{0}C. As both pressure and system subcooling increase, the minimum in the reflectivity curve appears to shift to lower Q values.
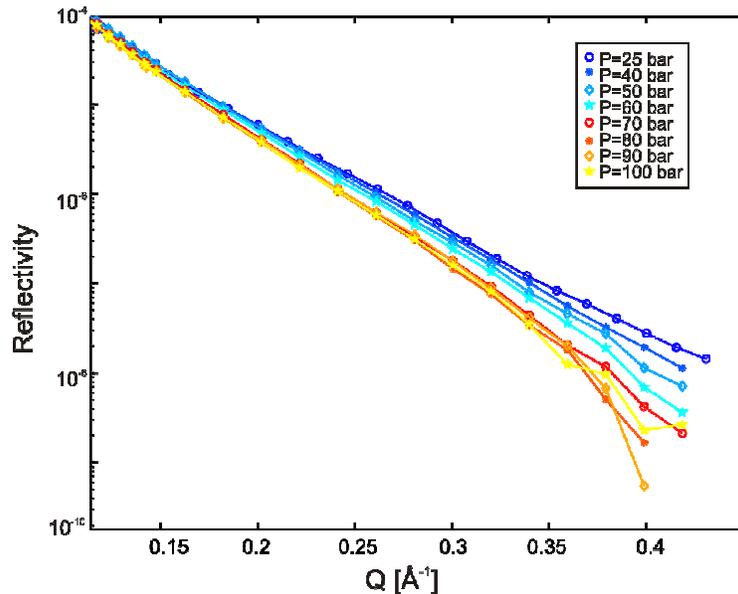
Figure 4: high-Q part of the reflectivity curves measured as a function of increasing pressure, for T=10°C. Outside the hydrate stability region as the pressure increases the reflectivity drops (blue to cyan curves). When the pressure rises above the hydrate formation pressure, P$_{eq}$=70bar for T=10°C, the interface stabilises (red to yellow curves).
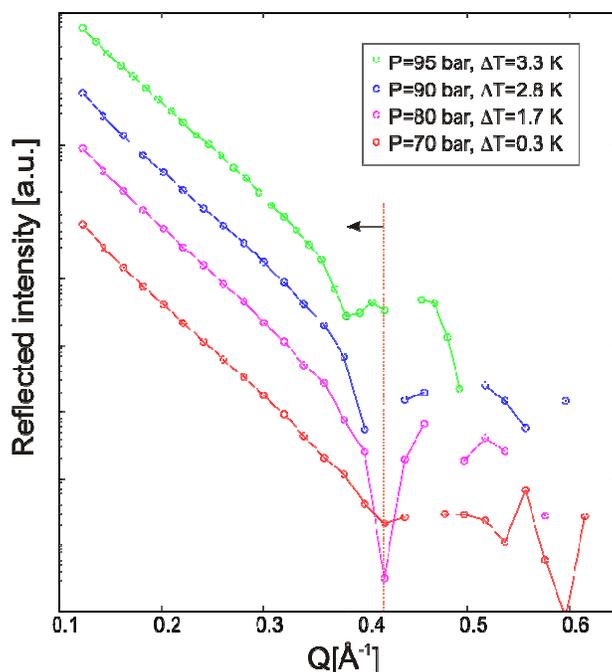
Figure 5. Curves measured at low subcoolings as a function of increasing pressure. The data are shifted vertically for clarity. For high Q values the data suggest the appearance of a layer. As the driving force increases (from bottom to top) the minimum of the curves shifts to lower Q values (see arrow), indicating an increase in layer thickness.

Discussion

With regards to the data presented in Figure 4, we believe that the observed stabilisation of the interface, when crossing the phase boundary by increasing the pressure, indicates that the optimum water-methane mixing required for hydrate nucleation has been reached. Unfortunately, within the allocated beam time, it was not possible to cross the phase boundary also under isobaric conditions. Without running the risk of an excessive speculation, we expect the reflectivity signal measured under isobaric conditions to show a similar behaviour to the one displayed by it's isothermal counterpart: a gradual change in electron density upon approaching the phase boundary, followed by a stabilisation once the stability region had been reached. Support for this hypothesis comes from the data presented in Figure 3: the investigated (P, T) conditions place the system well within the methane hydrate stability region and the data show neither a temperature nor a time dependence. The preliminary conclusions are therefore twofold. First of all, the results presented in Figure 4 may well represent the first microscopic evidence of a metastable state that acts as a precursor to hydrate nucleation. The data appear to indicate that the system is *ready* for nucleation and simply *waiting* for it occur. Most importantly, however, on the time scale of our observations, nucleation was not detected. This brings us to the second conclusion: hydrate nucleation appears to be a highly heterogeneous process. In as much, given a clean experimental apparatus as the one used during this experiment, higher driving forces than the ones that can be reached with our pressure cell are necessary to trigger methane hydrate nucleation. In order to further clarify these recent observations, the investigation of the gas/water interface for

other hydrate forming gases, whose stability regions overlap with methane, is of paramount importance. Finally, the data presented in Figure 5 show a very interesting trend and possibly the first experimental evidence of a layering effect that takes place within the methane hydrate stability region. However, in order to clearly confirm this, a detailed data analysis needs to be performed.