HD-73: Study of High-Pressure High-Temperature fluid carbon dioxide by inelastic x-ray scattering -- Allocated time: 18 shifts at ID16

High-pressure high-temperature fluid carbon dioxide was studied by inelastic x-ray scattering using the Si (999) reflection. The first aim of the experiment was to study the pressure dependence of the relaxational dynamics in a dumbbell system (linear non-polar molecules with quadrupolar interaction), i.e. in a class of molecular systems unexplored yet. The measurements were performed on samples loaded in diamond anvil cells. The temperature was set at 451 K in order to have a larger pressure range for the liquid phase.

An important part of the allocated beamtime was spent in order to optimize the experimental procedure, and especially to solve the difficult problem of the empty cell subtraction. Indeed, for single crystal samples, it is enough to reduce the disturbance induced by the scattering from the diamond anvils by properly orientating them; conversely, if one deals with a liquid sample, and especially if it is a light compound, the knowledge of the scattering contribution from the diamonds to the elastic line becomes crucial for the viscoelastic analysis. Once this analysis can be reliably performed, important parameters, such as the longitudinal viscosity, can be extracted from the measured spectra. In order to understand the empty cell contribution and its possible pressure dependence, we collected IXS spectra not only from the empty cell, but also from the solid sample at 3 GPa and 451 K. The comparison between the two cases revealed that the empty cell signal does not depend on pressure, at least in the pressure range explored in this experiment.

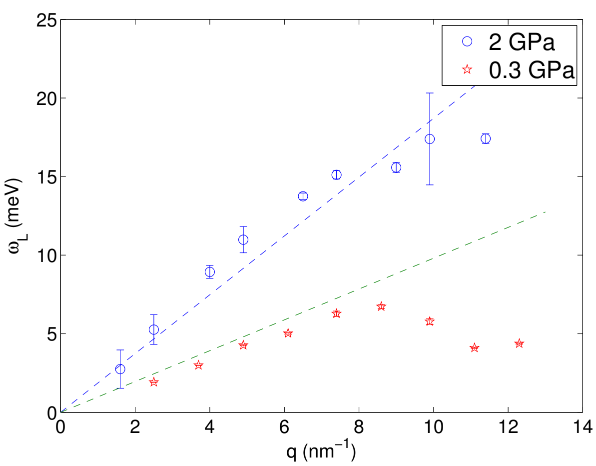

Figure 1: **Longitudinal sound dispersion compared with the acoustic dispersion expected from Brillouin sound velocity (dashed)**

We collected IXS spectra on the fluid at two pressures, 0.3 and 2 GPa, the latter being close to the freezing point. Two sets of exchanged momentum q were measured at each pressure, between 1.5 and 14nm^{-1}, for an integration time of 500 and 360 s respectively per energy point.

The low pressure data could be only fitted by a DHO model, giving a negative dispersion with respect to the Brillouin sound velocity. However, this result might be strangely affected by pressure drifts that were observed during measurements. Conversely, the high pressure data allowed for a viscoelastic analysis. The empty cell contribution to the elastic line turned out to be dominant at this pressure, so that after its subtraction the elastic line was drastically reduced. We analysed the data both before and after this operation and found that only by carefully subtracting the empty cell it was possible to obtain reliable fitting parameters. The elastic line was larger than the resolution function, giving evidence of the presence of a structural relaxation. The spectra were thus fitted to a model with two relaxation times. We found a marked positive dispersion in the longitudinal current velocity (cfr Figure), with respect to the Brillouin sound velocity (2.8 km/s). This is in agreement with Gorelli *et al.*'s prediction of a positive dispersion in all the supercritical fluids at P-T conditions lying above the Planck-Riedel curve[1]: at 451 K the intersection with this curve is at 0.05 GPa.

More importantly, from our analysis we could extract the longitudinal viscosity at 2 GPa and 451 K and found a value of ~2 mPa s, which is consistent with low pressure literature data on the bulk and shear viscosities [2].

[1] F. A. Gorelli et al. Phys. Rev. Lett. 97, 245702 (2006)

[2] K. Rah and B. C. Eu, J.Chem.Phys. 114, 10436 (2001) and 112, 7118 (2000)).