Experimental report

01/03/2022

Proposal: 6-02-611 **Council:** 4/2020

Title: Structure of supercritical CO2 between 0 and 100°C and, for pressure between 50 and 250 bar: data about nearest neighbours

Research area: Materials

This proposal is a new proposal

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Samples: Carbon dioxide

Instrument	Requested days	Allocated days	From	To
D4	8	0		
D16	4	4	01/02/2021	05/02/2021

Abstract:

SuperCritical CO2 fluids have become increasingly used by many industrials. A first series of experiments demonstrated that the results exhibit a contribution at small angles around Q < 0.1 Å-1. In addition to the small-angle scattering signal, an additional oscillation is visible in the 0.4-0.5 Å-1, which will help to discriminate between different models. At large angles, a broad maximum is visible and seems to be composed of two contributions. Their relative intensity and position vary significantly depending on P and T. Experiments (6-02-606) will be performed on D11 for the identification of any lamellar type structure in some (P,T) region. Based on the CO2 geometry (‘diameter/length’ ratio of about 2.6) and on its polarization, it is supposed that these two aspects are the organizing principles of the global molecular arrangement that will be seen with D11. The goal of the present proposal (in the continuity of 6-02-591 and 6-02-606) is to gain basic data about nearest neighbours distance and number of first nearest neighbours on D4. Moreover, we wish to complete data on small/large angle on D16 for gaining data about the liquid structure for a reference for the model.

***Report for Proposal 6-02-611 ILL*, D16**, 05/02/21-11/02/21: Structure of supercritical CO_2 between 0 and 100°C and, between 50 and 250 bar: data about nearest neighbours

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Introduction

The goal of the proposal was to performed neutron diffraction data on D16 for the CO_2 in the different fluidic states (liquid and supercritical) with various P&T conditions for completing data already gained with previous measurements (proposal 6-02-591).

A completely new experimental set-up was designed and built in order to have an accuracy and a precision better than 0.1 bar. Moreover, the set-up has a very high reactivity for the achievement of the constant chosen pressure: this allows a very good pressure stability during the diffraction experiments. Moreover, this system (with a high accuracy and stability) allows the exploration of the region closer to the critical point (CP: ~74 bar, ~31°C) where the heat capacity and the fluid density change rapidly with P&T. Moreover, with this new experimental set-up, it was possible to check experimental reproducibility with very good stability from one experiment to the others. Pressure stability is obtained with the help of a finely graduated syringe: any pressure variation is thus compensated with a volume variation that can be registered. The structure of the different fluidic CO_2 state can be studied making reference to any volume variation, or not. Even this volume variation is, at present, the sum of the cell volume and the one of the whole circuit between the pressure control system by the syringe and the cell where the measurements are performed, this allows an understanding of the dynamic and static of the fluidic state structures.

The starting data concerning the macroscopic parameter where obtained from [1]: these data (such as density, Cp, …) are the result of optimized equations of state identified from various data. These optimizations were built on a fitting minimization based on polynomial functions. These results are supposed to correspond to a stable fluid structure (or thermodynamic stability). But, some molecular or atomic structures can be dependent on the kinetic leading to these structures (for instance, the amorphous state for solid). It should be recalled that for SC-CO_2, different levels of property can be measured with the same density (but at different P&T) and, the same level of properties can be observed with different densities (still at different P&T). The conclusion of that comment is that other structural parameters have to be taken into account, as there is no bijective relationship between heat capacity and density for instance. The structural description will have to take in charge this aspect. It was to performed neutron diffraction measurements on state having the same density but for different P&T, in order to see if the neutron diffraction spectra were different on the same iso-density lines. Moreover, a broad range of density exists only in the supercritical state (between 350kg/m^3 and 600kg/m^3). Thus, the other question that orientates this research is, why this range of density can only exist above the critical pressure of ~74 bar and the critical temperature of ~31°C ? (These aspects about density are presented in figure 2 of the text for the submission of the proposal).

Experiments

The relative location of the P&T points measured on the mixture for the neutron diffraction experiments are reported in Figure 1 together with the data gained on SC-CO_2 with previous proposal (July 2019). The points of the same colour are positioned on iso-density line.

Results

The next figures give the neutron diffraction spectra for different densities (only spectra with the best-targeted density are reported here): 350kg/m^3, 470kg/m^3 and 600kg/m^3 correspond to the supercritical state and, 750kg/m^3 corresponds to the liquid state.

Comments and conclusion

In the liquid state (i.e. the highest density), which corresponds to a close contact between molecules, there is no real difference between the curves in the high angle domain (Figure 5), but differences appear in the small angle domain where the highest intensity is observed for the lowest temperature. Thus, at constant density, the structural parameter that induces

this difference in the small angle, 'concentrates' the beam light. In the supercritical state (i.e. in the density region that cannot exist in the gas and liquid state), the low and high angle show differences. The differences increase from high density towards low one: but in the high angle domain, the 'intensity bump' vanishes with decreasing density. There is a need for data in the molecular nearest-neighbours domain in order to understand exactly what is the 'concentrating beam light structure'. Moreover, we believe that these molecular nearest-neighbours structure should induce the structure at greater scale. The data will be first treated with Ornstein-Zernicke type model associated to Density Functional Methods and Molecular Dynamic approach for evaluating their modelling potentiality for SC-CO_2.

References

[1]- E.W. Lemmon, M.L. Huber, M.O. McLinden, *Reference Fluid Thermodynamic and Transport Properties - REFPROP*, Version 9.0, 2010.

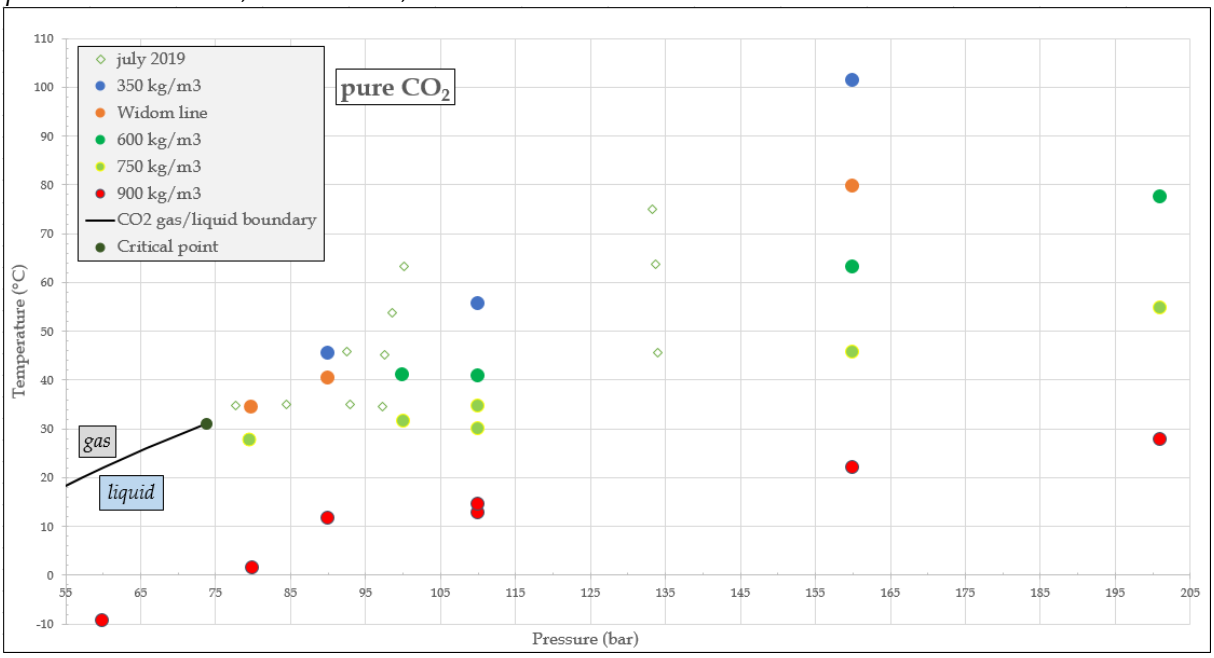

Figure 1: P&T position for the neutron diffraction data gained during that experiment. Two kinds of experiments are reported: 1) the data obtained with the first proposal (6-02-591), 2) with this proposal (6-02-611). The P&T positions were well controlled during the 2nd series of experiments and the stability of the P&T parameters was much better than in the preceding proposal (july 2019).

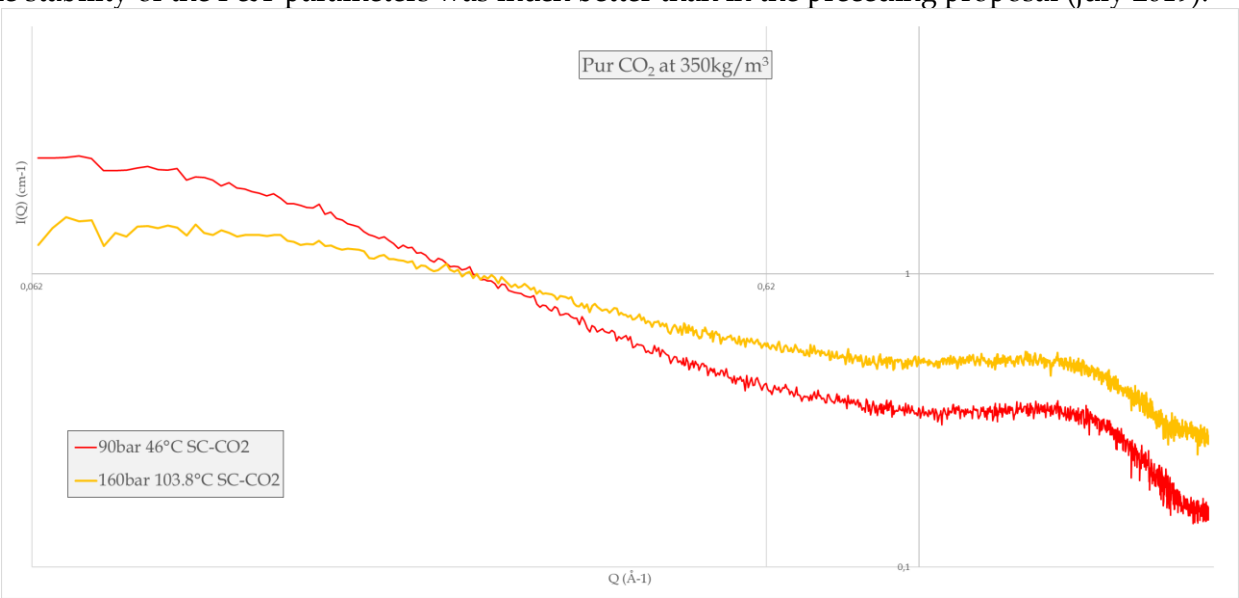

Figure 2: 350kg/m^3 CO_2, in the supercritical state.

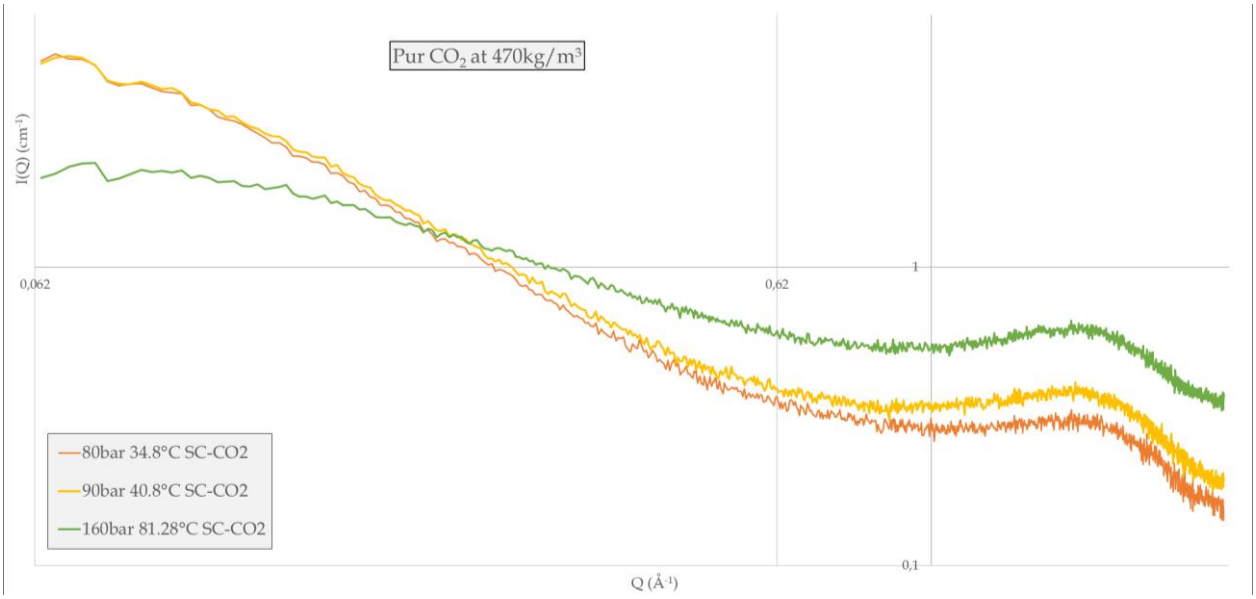

Figure 3: 470kg/m^3 CO_2, in the supercritical state.

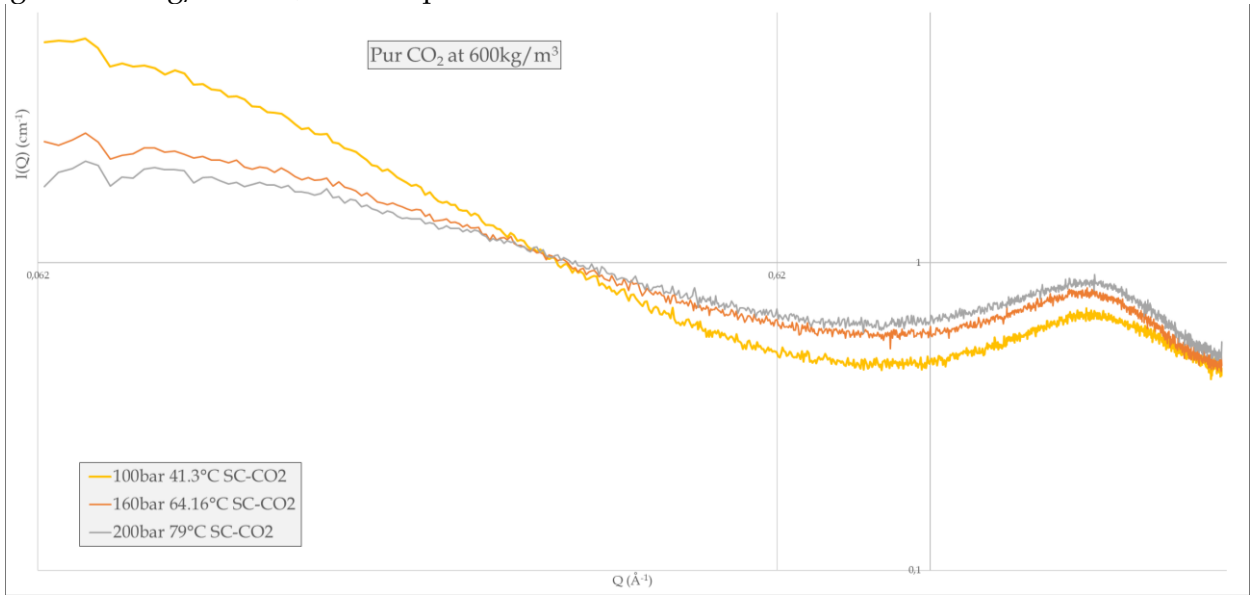

Figure 4: 600kg/m^3 CO_2, in the supercritical state.

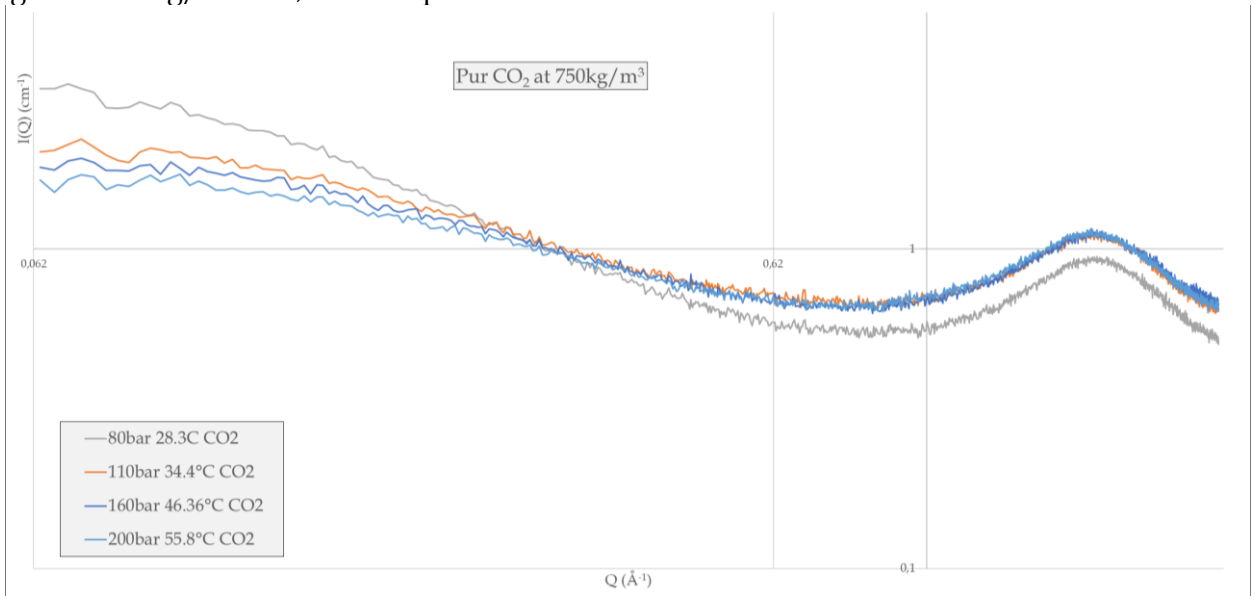

Figure 5: 750kg/m^3 CO_2, liquid state. The grey curve is shifted, the high angle 'bumps' are the same.