Experimental report

07/09/2022

Proposal: **6-02-606** **Council:** 10/2019

Title: Structure of supercritical CO2 between 0 and 100°C for pressure between 50 and 250 bar

Research area: Materials

This proposal is a continuation of 6-02-591

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Samples: Carbon dioxide

Instrument	Requested days	Allocated days	From	To
D16	4	0		
D11	3	2	17/03/2021	19/03/2021
D4	7	0		

Abstract:

SuperCritical fluids based on CO2 have become increasingly used in many industrial sectors as they can lead to a drastic reduction of water consumption and, of expensive or toxic chemicals.
A first series of neutron diffraction experiments demonstrated that the results exhibit a clear 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 be helpful to discriminate between different possible models. At large angles, a broad maximum is clearly visible and seems to be composed of two contributions. Their relative intensity and position vary significantly depending on P and T conditions.
The goal of the present project (in the continuity of the preceding one) is to base further analysis on 'pure liquid'; CO2 structures:
- below the critical T of about 31°C, for pressure below and above the critical pressure,
- above the critical T, for pressure well above 200 bar, where the SC structure seems to be homogenised.

The 'pure liquid'; structure will be the starting point for the validation and understanding of the SC-CO2 structure where the two phases seems

06/09/2022

Report for Proposal 6-02-606, D11, 17/03/21-19/03/21

Structure of supercritical (SC) CO_2 between 0 and 100°C for pressure between 50 and 250 bar.

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Introduction

Several data were obtained at high and low angles on D16 from ~3° to ~130°, with a wavelength of 4.5Å, (proposal 6-02-611), which corresponds to a range from 0.06 to 2.53 for Q ($Å^{-1}$). With D11, the range of measurement was between 0.014 to 0.24 Q ($Å^{-1}$), corresponding to an angle interval of about 0.38°-6.6° with a wavelength of 6Å. The set-up for injecting the CO_2 in the diffraction-measuring cell has a high thermal stability and accuracy is described in the reports up-loaded for the other proposal (6-02-611 and 6-02-607).

The data concerning the macroscopic parameters where obtained from [1]: these data (such as density, heat capacity C_p, …) are the result of optimized equations of state identified from various experimental data. These optimizations are based on a fitting minimization based on polynomial functions. These results are supposed to correspond to a stabilisation of the fluidic structure (thermodynamic stability). But some molecular or atomic structures can be dependent on the kinetic leading to these structures (for instance, the vitreous or amorphous state for solid).

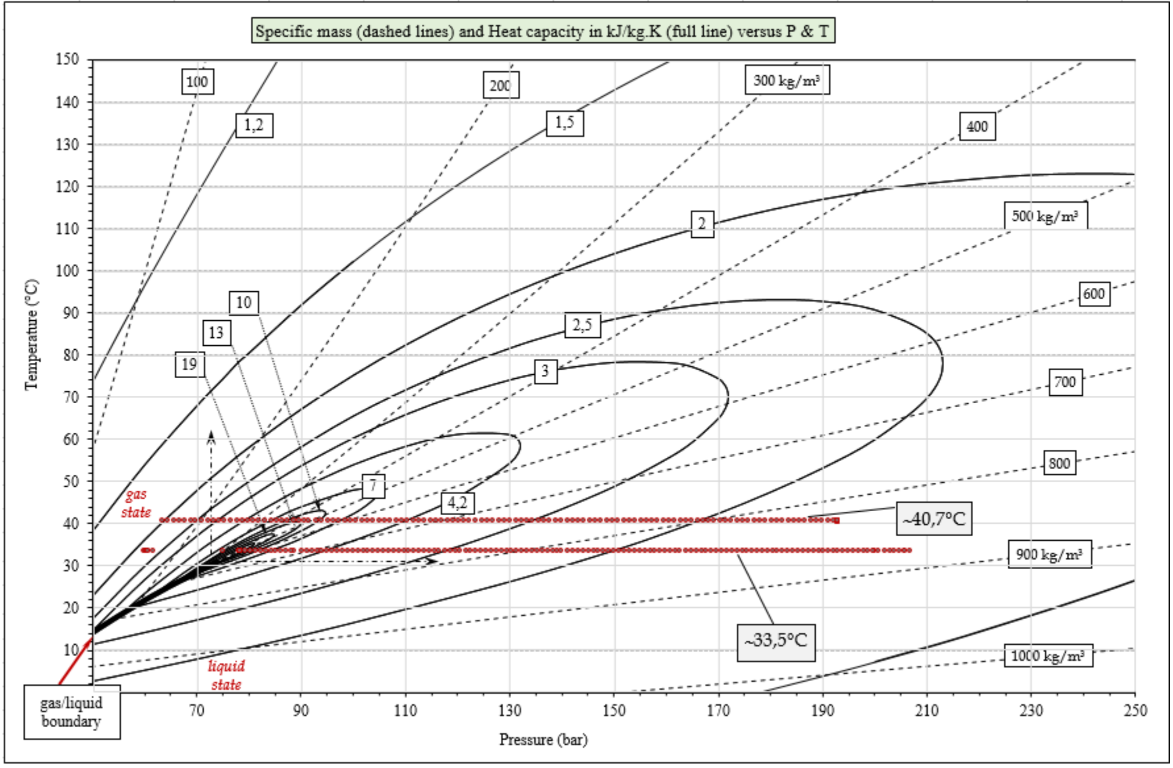

Figure 1: specific mass (dashed lines) and heat capacity (full line) are given as a function of P&T (calculated from [1]). These curves are reported for specific values for clarity. The two ramps (at constant T) are reported with red dots, each dot corresponds to a pressure maintained 6 to 7 minutes for the diffraction data acquisition.

It is generally considered that each value of a specific property would correspond to an atomic or a molecular arrangement with any possible adaptation(s) of these entities (i.e. in harmony with the global arrangement). But regarding Figure 1, it appears that, especially in the SC domain, (1) different heat capacity (C_p) can be observed with the same specific mass (but at different P&T) and, (2) the same level of heat capacity (C_p) can be observed with different specific mass (still at different P&T). Indeed, for case (1), the same specific mass curve (given by dashed straight lines in Figure 1) intersect the heat capacity elliptic curves several times and for case (2), a same heat capacity elliptic curve intersects several specific mass lines. From a theoretical point of view, the heat capacity of a crystalline solid (rather at low T) is a function of phonon vibrations [2]: the characteristics of phonons (a property of the atomic connections) are a function of the number of the first nearest-neighbours, i.e. thus a function of the number of atoms per unit volume. If a similar theory has to be derived from the solid and applied to the liquid state, the explanation of identical C_p with different specific masses (i.e. atoms per volume) or different C_p with identical specific masses remains to be proposed. Even data about first nearest-neighbours[1] have to be obtained for a basic description, it may be not sufficient for a theoretical description of C_p. The goals of this series of experiments were of three sorts:

- To enlarge the record about the molecular arrangement in the very low angle domain, looking for an eventual anisotropic structure (as a completion of the diffraction data obtained with D16). Indeed, as the CO_2 molecule is elongated with polarized bonds (Figure 2), it can be then supposed that some adjacent configurations could exist, or not, leading to possible organised structures at the global molecular arrangement as a function of intermolecular distances.
- To check the stability and/or evolution of the molecular arrangement over time.
- To have data with various densities in order to identify any structural differences, or not, leading to the same magnitude of macroscopic properties (such as heat capacity, viscosity, …).

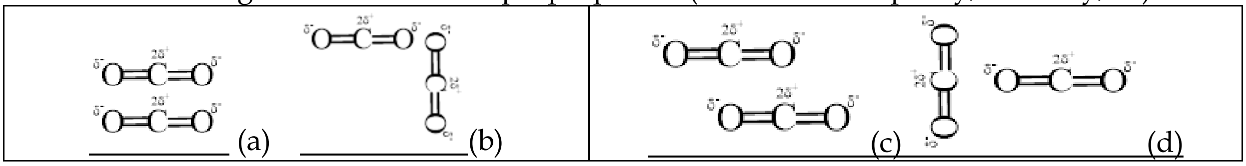

Figure 2: examples of CO_2 improbable molecular arrangement (a and b) and, of probable ones (c and d). These structures are encountered at an intermolecular distance to be identified. The arrangements reported are based on a planar description: the 3D improbable/probable states can be derived from these 2D schemes.

Experiments

Two kinds of experiments were performed:

- Ramps & plateaus: the ramp-experiment procedure was: 1) the temperature was kept constant (at 33.5°C and 40.7°C), 2) a starting pressure was of about 200bar, 3) the pressure was decreased with a step of ~1bar, 4) at each step, the pressure was kept constant for the duration of the diffraction acquisition. The decreasing pressure started from 202bar for the 1st ramp and, from 188bar for the 2nd ramp, and finished at ~60 bar for the two ramps.
- Two P&T static points (with the recording of several diffraction spectra with these conditions) were performed at:
  - 1) 60bar and -10.8°C (liquid state), these conditions are far from the CP with a low heat capacity (C_p ≈2.17kJ/Kg.K) and a high specific mass (1006kg/m^3);
  - 2) 78.15bar and 33.5°C (supercritical state), these conditions are close to the CP with a high heat capacity (C_p ≈52kJ/Kg.K) and an intermediate specific mass (476kg/m^3).

Results

- 1) Data gained with the 2 ramps & plateaus: it was chosen several pairs of P&T conditions (*'mirror points'*), leading to, A) the same specific mass (noted ρ in the tables below), and B) the same C_p. Spectra presented, left and right, in Figure 3 correspond to *mirror points* given respectively in Table 1 and Table 2. It appears clearly that the spectra for which the specific mass is (about) the same, are different: the C_p is different for the same density, leading to the idea that the atomic density (or the number and distance of first nearest-neighbours) is not sufficient for rendering the diffraction intensity (Q) and for describing C_p. The spectra for iso-C_p at 2 different temperatures are different: two same C_p have different densities leading to the idea that, again, C_p is not strictly dependent on atomic arrangements.
- 2) Data gained with the two static points (example in Figure 4): the measurements were performed when the P&T conditions were reached and stable for this two parameters. During the acquisition, the system had to adapt the CO_2 quantity in order to keep the P&T conditions targeted: during this matter adaptation operation, the density has certainly slightly changed. In order to understand what was the mechanism during this adaptation, a parallel image can be proposed. When a bucket is filled with dry sand, shaking the bucket help to increase the density and supplementary quantity of sand can be added in the bucket. At some point, the repetition of the operation leads to a state where it is not any more possible to add some sand. Shacking is necessary. An interpretation of this CO_2 addition in the cell can be proposed. When the experimental cell is filled with CO_2 in order to reach the P&T conditions, the CO_2 arrangement is not optimal. The mechanism of density increase at constant P&T would

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[1] The proposal on that point was not accepted for the last ILL run.

correspond to an *auto-organisation phenomenon* whose '*engine*' would be based on the existence of the polarized zones of the CO_2 molecules, whose intermolecular arrangement is the results of molecular motions '*pushed*' by the first local optimal arrangements from near to far, local steps by local steps.

P(bar) at 33,53°C (measured)	C_p (kJ/kg.K) calculated	ρ (kg/m³) calculated	ρ (kg/m³) (target)	ρ (kg/m³) calculated	C_p (kJ/kg.K) calculated	P(bar) at 40.7°C (measured)
133.25	2.70	802.2	802	802.5	2.47	169.2
91.94	4.53	700.7	700	699.9	3.67	116.8
81.11	10.85	609	608	607.4	6.25	99.3
80.02	14.90	583.9	584	585.6	7.19	97.2

Table 1: 'mirror' iso-density points. REFPROP [1] was used for the calculated value. (see left spectra Figure 3).

P(bar) at 33,53°C (measured)	ρ (kg/m³) calculated	C_p (kJ/kg.K) calculated	C_p (kJ/kg.K) target	C_p (kJ/kg.K) calculated	ρ (kg/m³) calculated	P(bar) at 40.7°C (measured)
122.5	784.5	2.88	2.87	2.88	214.3	73.07
109.6	758.1	3.24	3.22	3.22	228.9	75.2
99.8	731.1	3.73	3.74	3.75	247.7	77.54
92.9	704.5	4.4	4.4	4.4	267.2	79.65
88.0	679.5	5.31	5.31	5.31	290.1	81.73
83.1	638.1	7.81	7.85	7.86	340.7	85.2
81.11	609	10.85	11.7	11.66	411.1	88.45

Table 2: 'mirror' iso-C_p points. REFPROP [1] was used for the calculated value (see right spectra Figure 3).

Conclusions: 1) spectra at iso-density and at iso-C_p obtained for different pressures for two different temperatures show that an arrangement description based on the molecular relative localisation is not sufficient for rendering, the difference of properties at constant density or, the constancy of properties with changing density. 2) the auto-organisation phenomenon based on the presence of polarised zone can explain the change of diffraction spectra at constant P&T conditions (see text for explanation).

References

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

[2]- G. Burns, Solid state physics, Editions Academic Press, 1985-1990, p.362-369.

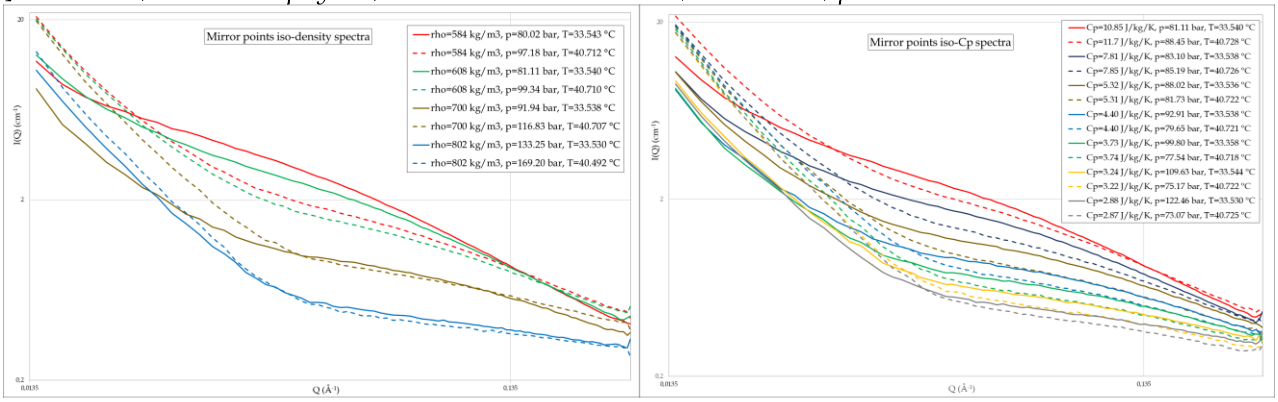

Figure 3: Left) iso-density spectra at 33.5°C and 40.7°C. Right) iso-C_p spectra at at 33.5°C and 40.7°C.

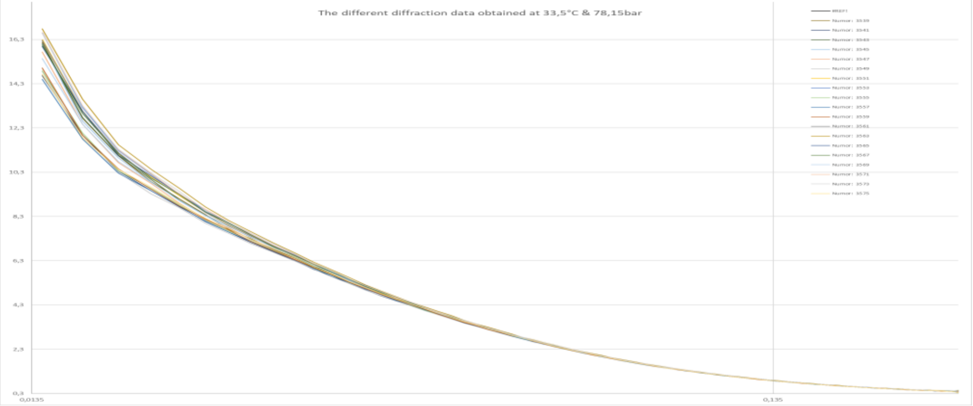

Figure 4: an example of diffraction data at the same P&T conditions (78.15bar - 33.5°C (supercritical state).