Abstract. In situ neutron diffraction measurements of adsorbed carbon dioxide in an ordered mesoporous silica (MCM-41) have been carried out along an isotherm slightly above the critical point (308 K) and at a range of pressures below and above the critical one (30-125 bar). The experiment has been performed with the aid of a novel high-pressure adsorption apparatus and the GEM diffractometer (ISIS, Rutherford Appleton Laboratory, UK). Diffraction measurements of both bulk supercritical and bulk liquid carbon dioxide have also been carried out. The structure factors and the total differential correlation functions of the adsorbed carbon dioxide suggest that the confined carbon dioxide has liquid-like properties. However, some differences are observed when the confined phase is compared to those of bulk liquid and bulk supercritical fluid respectively, mainly arising from orientational correlations between adsorbed molecules. These differences could be attributed either to strong interactions between the silica walls and CO$_2$ molecules or to the confinement of the fluid combined with the relatively large quadrupole moment of carbon dioxide.

1. Introduction

Supercritical fluids are gaseous compounds, which are compressed to a pressure higher than the critical pressure ($P_c$) above their critical temperature ($T_c$) and have nowadays been attracting scientific as well as industrial interest because of their unusual physical properties, since their density can vary significantly even with a slight change of the temperature and pressure. Based on these properties, supercritical fluids, supercritical fluids are widely used in industry as solvents for extraction and for chemical and biochemical reactions. [1-3]. In many cases carbon dioxide, the simplest liquid composed of linear molecules, is the solvent of choice because it is environmentally benign, abundant, inexpensive, non-flammable, non-toxic and its supercritical state is easily accessible with a $T_c$=304.1 K and $P_c$=73.8 bar. On the other hand, sorption of fluids on nanoporous solids is very important in a series of applications such as catalysis, H$_2$ and natural gas upgrade and storage, chromatographic pressure swing adsorption and membrane) separations, biological and geological processes etc. [4-6]. These processes are extremely complex from a fundamental point of view as the properties of sorbed
fluids are different from the bulk due to confinement. As a result, there is an increasing interest in the experimental study of fluids confined in nanoporous materials [7-10].

Adsorption measurements [11] are abundantly used for the study of pore-confined fluids, however such methods can only reveal the statistical "ensemble" macroscopic properties and do not provide information on their molecular structure. On the other hand techniques such as small-angle scattering (SAS) of x-rays or neutrons (SAXS, SANS) [12-16], contrast-variation or contrast-matching SANS [17-26] are essential tools for elucidating the microstructure of nanoporous materials and for resolving structural characteristic of each phase in multiphase materials. Further, adsorption in conjunction with in situ SAS or diffraction can provide in depth information about both the adsorption mechanism and the structural organisation of the confined phase [27-41].

In the present study in situ neutron diffraction measurements of CO$_2$ confined in a purely siliceous MCM-41 have been carried out along an isotherm slightly above the critical point (T=308 K) and at a range of pressures below and above the critical one (30, 50 and 125 bar respectively). Furthermore, neutron diffraction measurements of both bulk supercritical and bulk liquid CO$_2$ thermodynamic states have also been performed. For this reason, a high-pressure adsorption apparatus has been constructed. MCM-41 is an ideal candidate for adsorption studies because it consists of a two-dimensional hexagonal arrangement of cylindrical mesopores with uniform size.

2. Experimental

The adsorption/neutron diffraction experiment was carried out at General Materials diffractometer (GEM), at ISIS pulsed neutron and muon source (UK Rutherford). GEM is one of the most advanced materials diffractometer in the world. The most important reason in achieving this has been the detector array, which has a very large area of 7,270 m$^2$ and a very wide range in scattering angles corresponding to a $Q$ range varying between 0.02 Å$^{-1}$ and 40 Å$^{-1}$. For a full description of the diffractometer, see ref 42.

![Figure 1. High-pressure adsorption device for carrying out in situ neutron diffraction measurements.](image-url)

A high-pressure adsorption device (high vacuum up to 150 bar) has been constructed for performing in situ diffraction measurements (figure 1). A thin wall cylindrical titanium zirconium (Ti/Zr) null scattering alloy, having an overall nominal coherent scattering length of zero, was used as sample container. The cell was connected via a copper flange and a Swagelok® union to a 1/8” (OD) 316 SS capillary. The set-up is inserted in a CCR (close-cycle-refrigerator) stick and connected to a
The synthesis and the structural characteristics of MCM-41 based on powder x-ray diffraction, N\textsubscript{2} and CO\textsubscript{2} adsorption isotherms can be found elsewhere [47-48]. In brief, the specific surface area and the total pore volume have values 1204 m\textsuperscript{2}/g and 0.87 cm\textsuperscript{3}/g respectively. The unit cell parameter is approximately 40 Å\textsuperscript{-1} whereas the mean pore radius was estimated to be 12 Å according to BJH (Barrett–Joyner–Halenda) method and 17.5 Å according to non-local density functional theory (NLDFT) method.

The structure factor of bulk liquid CO\textsubscript{2} is shown in figure 2 (top curve). The intermolecular structure peak is located at about 1.79 Å\textsuperscript{-1}, whereas a long range oscillation corresponding to intramolecular correlations is observed at larger Q values. The main diffraction peak has a minimum at Q~3 Å\textsuperscript{-1} followed by a tiny bump near 4 Å\textsuperscript{-1}. The results are in excellent agreement with previous similar neutron diffraction measurements of bulk CO\textsubscript{2} [49-50]. It is worth mentioning that in some cases (e.g. 220 K, 58 bar) a shoulder has been observed on the high Q side, (Q~2.2 Å\textsuperscript{-1}), of the main diffraction peak [50]. Based on theoretical calculations, Gubbins \textit{et al} [51] attributed the origin of this feature to the quadrupole-quadrupole contribution of the anisotropic part of the structure factor. Adya and Wormand [50] claimed that this hump is both temperature and density dependent. On the other hand, Chiappini \textit{et al} [52] argued that this feature was only density dependent based on neutron diffraction experiments of bulk carbon dioxide in dense supercritical states. In our case, such a shoulder is not expected due to the lower density of the bulk phase. The main peak possesses a degree of asymmetry, which can be attributed to intermolecular orientational correlations between neighbouring CO\textsubscript{2} molecules arising mainly from electrical quadrupolar interactions. In particular, Chiappini \textit{et al} [52] performed diffraction experiments on bulk supercritical CO\textsubscript{2} under high pressures and they also observed a strongly asymmetric main peak. By comparing their data with a calculated intermolecular structure factor for an orientationally uncorrelated model CO\textsubscript{2}, they concluded that the asymmetry of the peak is due to the existence of the orientational correlations. In addition, the structure factor of the bulk supercritical fluid has many similarities to that of the bulk liquid. The main peak asymmetry, the minimum at about 3 Å\textsuperscript{-1}, the tiny bump at Q~3.7 Å\textsuperscript{-1} (to a less extent) and the long range intramolecular peaks are also present. One should note, however, that the position of the main peak has shifted slightly to lower angles (Q~1.74 Å\textsuperscript{-1}) due to the fact that the supercritical fluid has lower density than that of the liquid.

The structure factors, for the confined fluid at 30, 50 and 125 bar are also presented in figure 2. As in the case of bulk thermodynamic states, the patterns exhibit clearly a peak corresponding to the most probable distance between nearest neighbour molecules, while the long range oscillations at larger Q values are also present. The peak position shifts slightly to the higher Q region with increasing
pressure and reaches that of the bulk supercritical fluid. As in the case of the bulk states, the main peaks of the confined CO$_2$ have a minimum at about $Q=3 \text{ Å}^{-1}$. The structure factors of adsorbed CO$_2$, however, exhibit additionally a shoulder, $q_1$, on the high $Q$ side of the peak ($Q\approx 2.7 \text{ Å}^{-1}$) followed by a more enhanced bump, $q_2$, at lower scattering vectors ($Q\approx 3.5 \text{ Å}^{-1}$) compared to the one observed at the bulk liquid. One should also mention that both features are mostly pronounced at 30 bar and to a less extent at 50 bar (figure 2b). A possible explanation is that at lower pressures the scattering is dominated by the adsorbed monolayer. This argument is further enhanced by the fact that these features have also been observed for carbon dioxide adsorbed in the same material at a subcritical thermodynamic state ($T=273$ K, $P=5$ bar) corresponding to monolayer coverage [48]. The confined phase seems to be in a quasi-liquid state where orientational correlations are somehow enhanced. This might be attributed to the effect of Van der Waals and Coulombic surface landscape in combination with interactions between neighbouring CO$_2$ molecules directly attached to the surface.

Figure 2. The total-scattering structure factor for confined CO$_2$ (308 K) at 30 bar, 50 bar, 125 bar, for bulk supercritical fluid at 125 bar (308 K) and for bulk liquid at 19.7 bar (253 K); the order is from the bottom to the top. The structure factors have shifted by 0.3 for clarity. (a) the whole $Q$ range and (b) the low $Q$ region.

Figure 3 illustrates the total differential correlation function, $D(r)$, for all thermodynamic states (bulk and confined respectively). In all cases, one clearly observes two intramolecular peaks (completely separated from the intermolecular interactions) occurring at 1.16 Å and 2.32 Å which correspond to the C-O ($r_{CO}$) and O-O ($r_{OO}$) distances, with $r_{OO}=2r_{CO}$. Furthermore, the intermolecular part of all the correlation functions shows two broad features centered at ~4 Å and ~8 Å, arising respectively from the first and second neighbour interactions. In the case of bulk liquid CO$_2$, however, the first neighbour peak reveals three structures located at about $r_1=3.3$ Å, $r_2=4$ Å, and $r_3=5.2$ Å respectively (figure 3a), in agreement with literature data on bulk liquid CO$_2$ [50]. Molecular dynamics simulations have shown that the structure at $r_1$ is attributed mainly to O-O as well as to C-O pair correlations. Moreover, both C-C and C-O correlations give a positive contribution at $r_2$, while the
structure at \( r_2 \) arises from bumps present in the partial C-O and O-O atom-atom pair correlation functions, when quadrupole forces are included in the simulations [52, 53]. On the other hand, in the case of bulk supercritical fluid the structure \( r_1 \) is not present and there is also a slight shift of the position of the first neighbour peak at \( \sim 4.2 \, \text{Å} \) due to its lower density.

![Graph](image)

*Figure 3.* The differential correlation function for confined \( \text{CO}_2 \) (308 K) at 30 bar, 50 bar, 125 bar, for bulk supercritical fluid at 125 bar (308 K) and for bulk liquid at 19.7 bar (253 K); the order is from the bottom to the top. The correlation functions have shifted by 0.3 for clarity. (a) the whole real space distance and (b) details of the first neighbour region.

The molecular arrangement in confined states seems to be closer to that of the bulk supercritical fluid, however, certain differences are observed. First of all, the structure \( r_2 \) is narrower and a new feature is observed at \( \sim 4.6 \, \text{Å} \) for the confined carbon dioxide state at 30 bar. Further, the structure \( r_3 \) is more enhanced, especially for the confined fluid at 30 and 50 bar respectively (figure 3b). Again, \( r_3 \), was a prominent feature in the case of adsorbed \( \text{CO}_2 \) under subcritical conditions corresponding to the monolayer coverage [48]. Based on simulation results, this structure was proved to be strongly potential dependent, becoming evident only when electric quadrupolar interactions are taken into account and can be ascribed to a sharpening of the O-O correlations, arising from increased orientational ordering of the fluid [52]. This seems to be a plausible explanation, as at lower pressures the adsorbed monolayer is subject to enhanced Lennard-Jones and Coulombic interactions with the surface atoms. Based on this approach the silica surface seems to somehow organise the monolayer in a more “oriented” manner in order to counterbalance the strong adsorption potential with the finite size of the surface.

4. Conclusions

The structural characteristics of supercritical carbon dioxide molecules confined in a mesoporous MCM-41 material have been studied by sorption with *in situ* neutron diffraction measurements. For this purpose, a novel high-pressure adsorption device has been constructed and a diffractometer with a wide accessible \( Q \) range was selected. The structure factors of \( \text{CO}_2 \) and the total differential
correlation functions suggest that the confined fluid has at all stages studied liquid-like properties, however, some subtle differences pointing to stronger orientational correlations inside the pores were observed. These differences were attributed to either pore wall-fluid interactions or the confinement of the fluid, combined with the relatively large quadrupole moment of carbon dioxide. Sorption with in situ neutron diffraction provides an excellent tool to study confined phases within pores In addition, a future combination of molecular simulation approaches coupled with our results would throw more light in the molecular arrangement under confinement.

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