Structural characterisation of subcritical carbon dioxide confined in nanoporous carbon by \textit{in situ} neutron diffraction

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Abstract. \textit{In situ} neutron diffraction measurements of adsorbed carbon dioxide in an ordered mesoporous carbon (CMK-1) have been carried out along an isotherm at 253 K and at a range of pressures up to 18 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 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 fluid has \textit{liquid-like} properties at all thermodynamic states studied; however, some subtle differences were observed pointing to enhanced adsorption because of the presence of micropores.

1. Introduction

Sorption of fluids on nanoporous solids is very important in a series of applications, such as catalysis, H\textsubscript{2} and natural gas upgrade and storage (chromatographic pressure swing adsorption and membrane) separations, biological and geological processes etc. [1-3]. These processes are extremely complex from a fundamental point of view as the properties of sorbed fluids are in many cases different from the bulk due to confinement. For instance, confined geometries play significant role on first-order phase transitions and also in the glass formation [4]. For the above reasons there is an increasing interest in the experimental study of fluids confined in nanoporous materials [5], including phase transitions [6] and dynamical properties of liquids in nanometer-sized porous materials [7]. On the same ground, powerful theoretical and computer simulation techniques have been used for the study of adsorption in model nanopores [8-11].

On the other hand, adsorption measurements [12] 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) [13-17], contrast variation or contrast matching SANS [18-27] 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 [28-42]. The discovery of ordered mesoporous materials opened new opportunities in the synthesis of structured carbons using templating techniques [43]. In particular, CMK-1 is an ordered mesoporous carbon molecular sieve [44] prepared by using ordered mesoporous silica MCM-48 as a template after filling its pores with a carbon source (e.g. sucrose), which is pyrolysed resulting in the formation of rod-type carbon inside the silica channels. Upon silica removal, the remaining pure carbonaceous material has a porous texture consisting of a three dimensional regular array of uniform mesopores, also containing micropores in the mesopore walls [45]. In a recent study [46], the results of in situ neutron diffraction measurements of adsorbed CO$_2$ in a purely siliceous MCM-41 revealed that the confined phase has liquid-like properties. In the present study in situ neutron diffraction measurements of CO$_2$ confined in a purely carbonaceous CMK-1 have been carried out along along the same isotherm at 253 K. Furthermore, neutron diffraction measurements of bulk liquid CO$_2$ ($T=253$ K, $P=19.7$ bar) have also been performed.

2. Experimental

The material CMK-1 was prepared using MCM-48 template by a procedure involving impregnation with sucrose in the presence of sulfuric acid, followed by carbonisation and removal of the silica template [47]. More specific, 2 g of MCM-48 were added to a solution obtained by dissolving 2.5 g of sucrose and 0.28 g of H$_2$SO$_4$ in 12 g of H$_2$O. The mixture was placed in a drying oven for 6 h at 373 K and subsequently the oven temperature was increased to 433 K and maintained there for 6 h. The sample turned dark brown or black during the treatment in the oven. The silica sample, containing partially polymerised and carbonised sucrose at the present step, was treated again at 373 and 433 K using the same drying oven after the addition of 1.5 g of sucrose, 0.16 g of H$_2$SO$_4$ and 12 g of H$_2$O. The carbonisation was completed by pyrolysis with heating to typically 1173 K under vacuum. The carbon-silica composite obtained after pyrolysis was washed with 48 wt% hydrofluoric acid at room temperature, to remove the silica template. The template-free carbon product thus obtained was washed with H$_2$O and ethanol, redissolved with EtOH after centrifuging, poured on to a petri dish and dried at 393 K.

The N$_2$ adsorption isotherms have been performed volumetrically at 77 K on an Autosorb-1 gas analyzer, Micropore version (Quantachrome instruments). The CO$_2$ adsorption isotherm was measured at 253 K on an Intelligent Gravimetric Analyser (IGA). For adsorption measurements, the sample was initially outgassed at 300 °C for 12 h under high vacuum (<10$^{-6}$ mbar). For the gravimetric measurements, at 253 K an ice/NaCl bath was used. N$_2$ (99.999%) and CO$_2$ (99.995%) purchased from Messer-Griesheim were used directly from pressure reducer equipped gas cylinders.

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. For a detailed description of the instrument, see ref 48.

A novel high-pressure adsorption device (high vacuum up to 150 bar) has been constructed for performing in situ diffraction measurements and a thin wall cylindrical titanium zirconium (Ti/Zr) null scattering alloy was used as sample container (see refs 46 and 49 for a more extended discussion). After cooling down to room temperature the whole stick was inserted in the CCR, sample temperature was set to 253 K, and doses of CO$_2$ (99.9996%) were admitted, while equilibration was monitored by pressure readings. After measuring the diffraction spectrum at 18 bar, the sample was removed from the cell and measurements of empty cell as well as bulk liquid CO$_2$ were performed ($T=253$ K, $P=19.7$ bar).

The scattered neutrons were counted as a function of neutron time-of-flight for eight detector banks. The raw data were corrected for background, attenuation and multiple scattering and were normalised to a standard vanadium scatterer using the gudrun program [50-51]. Gudrun is preferred for this purpose because it takes into account the azimuthal detector angle, which is an important consideration for GEM. The Placzek inelasticity correction and the merging of data from different
detector banks, were performed using the ATLAS suite of programs [52]. Finally, the calculated structure factors were Fourier transformed up to $Q_{\text{max}}=15$ Å$^{-1}$ for the derivation of the differential correlation functions, using the Lorch modification function for reducing the termination ripples [53]; however, this gain results in some loss of resolution with $\Delta r_{\text{Lorch}}=0.36$ Å.

3. Results and discussion

3.1. Adsorption isotherms

Figure 1 shows the adsorption isotherms of carbon sample prepared, as well as that of MCM-48, used as template. The $N_2$ adsorption isotherm for MCM-48 is of type IV, according to the IUPAC classification [54]. At low pressures, a steep increase is observed due to the formation of a monolayer on the pore walls, while at higher pressures an extended multilayer region and a sharp pore condensation step can be observed. On the other hand, the isotherm of CMK-1 showed an initial sharp uptake followed by a steadily increase up to about $p/p_0=0.3-0.4$. The distinct adsorption step observed in MCM-48, in the relative pressure range of 0.2–0.3, disappeared and the nitrogen adsorption isotherms changed from type IV (MCM-48) to type I/II for CMK-1. According to the IUPAC classification, the type I/II isotherms may be often observed on microporous solids. The CMK-1 carbon only showed a small increase in the amount of adsorption at relative pressures higher than 0.30, mainly, due to adsorption on the wider pores and the external surface. In addition to the mesopores with diameter of 22 Å, the structure of CMK-1 contains abundant micropores, which were formed in the amorphous carbon framework prior to the removal of silica wall, while the mesopores were formed upon the removal of the silica wall. One should note that the isotherms of all samples exhibited an upturn at pressures close to the vapour pressure which can be attributed to large (presumably macro-) pores formed between the particles. Again, the absence of hysteresis loop in all isotherms is due to their pore size, lying between the margins of micro- and mesopore regions [55].

![Figure 1. $N_2$ adsorption isotherms at 77 K on CMK-1 and MCM-48 precursor respectively. Insert: Pore size distribution of CMK-1 using NLDFT method.](image-url)
The structural characteristics of CMK-1 including the specific surface area, the pore volume and the mean pore radius were determined from N$_2$ adsorption measurements at 77 K. A specific surface area, $S$, of 1760 m$^2$/g was determined by the BET (Brunauer-Emmett-Teller) method (surface area of N$_2$ molecules = 16.2 Å$^2$), while the total pore volume, $V_p$, equal to 1.02 cm$^3$/g, was derived from the amount adsorbed at $p/p_0=0.975$, assuming that N$_2$ has completely filled the pores in its normal liquid state (density =0.807 g/cm$^3$). Finally, pore size distribution was deduced by non-local density functional theory (NLDFT) [56] methods, revealed a bimodal pore size distribution (PSD), which range from 0.7 to 3 nm. Therefore, CMK-1 seems to have a PSD from micropores to small mesopores. Both large micropores (average size ~10-12 Å) and small mesopores (about 36 Å) are predominant in CMK-1. It must be noted that for the latter class of pores, the corresponding value obtained by BJH (Barrett–Joyner–Halenda) is about 22-24 Å. The average pore size obtained by BJH method is quite similar to that for MCM-48 using the same method, although it is quite different from the pore wall thickness of MCM-48 (ca. 10 Å) [57]. The observed changes can be attributed to the fact that the carbon precursor shrinks during carbonisation, giving rise to the greater pore width than the pore wall thickness of MCM-48 [57].

The CO$_2$ adsorption isotherm of CMK-1 at 253 K is shown in figure 2. The initial adsorption is due to the presence of micropores, while a gradual increase is obvious at higher pressures. The absence of a steep condensation step suggests a wider pore size distribution. Similar to N$_2$ isotherms no hysteresis loop was observed. Finally, the pore volumes calculated from N$_2$ and CO$_2$ isotherms are almost identical (Gurvitz rule is valid) indicating full accessibility of both molecules to the pore network.

![Figure 2. CO$_2$ adsorption isotherm at 253 K on CMK-1.](image)

3.2. Structural characteristics of confined carbon dioxide

The structure factor of bulk liquid CO$_2$ is shown as the top curve of figure 3. The intermolecular structure peak is located at about 1.79 Å$^{-1}$, while 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$^{-1}$ followed by a very tiny bump near 4 Å$^{-1}$. The main peak possesses a degree of asymmetry, which can be attributed to intermolecular orientational correlations between neighbouring CO$_2$ molecules arising mainly from electrical quadrupolar interactions [58]. The results are in excellent agreement with previous similar neutron diffraction measurements of bulk CO$_2$ [59-60]. It is worth
mentioning that in some cases (e.g. 220 K, 58 bar) [60] a shoulder has been observed on the high Q side of the main diffraction peak ($Q \sim 2.2 \text{ Å}^{-1}$). Based on theoretical calculations, Gubbins et al [61] attributed the origin of this feature to the quadrupole - quadrupole contribution of the anisotropic part of the structure factor. Adya and Wormand [60] claimed that this hump is both temperature and density dependent. Chiappini et al [58] 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.

Further, the structure factors of the confined carbon dioxide in CMK-1 at 10, 14 and 18 bar respectively are also presented at figure 3. 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 observed for the bulk liquid are also present although to a less extent. The peak position shifts slightly to the higher Q region with increasing pressure and reaches that of the bulk liquid at $P = 18$ bar. As in the case of the bulk liquid, the main peaks of the confined CO$_2$ have a minimum at about $Q = 3 \text{ Å}^{-1}$. One may note that the main peak of the confined phase possesses a lower degree of asymmetry compared to that of the bulk liquid. In addition, during all adsorption stages, the first intramolecular oscillation of the confined CO$_2$ has been slightly moved towards the low-Q regime. The most striking difference, however, is that the bump near 4 Å$^{-1}$ has become a prominent feature. This maximum has also been observed as a tiny bump for dense CO$_2$ thermodynamic states, such as bulk liquid close to the triple point [59-60] or supercritical fluid under very high pressures [58]. The observed densification can be explained by considering that within micropores, which are no more than a few molecular diameters wide, the potential fields from neighbouring walls overlap and produce a very deep potential well. As a result, the interaction energy between the gas molecules and the adsorbent matrix is increased and adsorption is enhanced while the adsorbed molecules within the confined pore space are arranged in very dense states to compensate the lack of free volume [33].

Figure 3. The total-scattering structure factors at 253 K for confined CO$_2$ at 10, 14 and 18 bar, respectively, and the total-scattering structure factor for the bulk liquid at 19.7 bar; the order is from the bottom to the top. The structure factors have shifted by 0.5 for clarity. (a) the low Q region and (b) the whole Q range.
Figure 4 illustrates the total differential correlation function, $D(r)$, for the confined CO$_2$ at pressures 10, 14 and 18 bar. The correlation function for the bulk liquid is also shown as the top curve. 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 $r_{OO} = 2r_{CO}$. Further, the intermolecular part of the correlation functions of the bulk liquid presents clearly two broad features centered at ~4 Å and ~8 Å, arising respectively from the first and second neighbour interactions. The first neighbour peak reveal three structures located at about $r_1$=3.3 Å, $r_2$=4 Å and $r_3$=5.2 Å respectively, in agreement with literature data on bulk liquid CO$_2$ [60]. Molecular dynamics simulations have revealed 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 $r_2$, whereas the structure at $r_3$ 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 [58, 62].

On the other hand the correlation functions of CO$_2$ confined in CMK-1 do not exhibit these three structures located at the first neighbour peak, although there is a tendency for the structure $r_3$ to appear at about 5 Å. Based on simulation results, this feature is 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 [58]. This seems to be a reasonable explanation, as the micropore filling is subject to enhanced Lennard-Jones interactions with the surface atoms. In addition, the main peak has been slightly shifted to larger distances (~4.2 Å) and does not seem to vary notably with increasing pressure. Further details about the molecular organisation of the confined phase can be deduced by advanced simulations in combination with our results obtained by the in situ diffraction measurements.

Figure 4. The differential correlation functions for confined CO$_2$ at 10, 14 and 18 bar, respectively, and for the bulk liquid; the order is from the bottom to the top. The correlation functions have shifted by 0.2 for clarity. (a) details of the first neighbour region and (b) the whole real space distance.
4. Conclusions
In conclusion, the structural characteristics of CO\(_2\) confined in an ordered carbonaceous material have been investigated by \textit{in situ} neutron diffraction measurements. Both the structure factors of confined CO\(_2\) together with the total differential correlation functions have been derived and have been compared to those of the bulk CO\(_2\) in liquid state. The results suggest that the confined fluid has \textit{liquid-like} properties at all thermodynamic states examined. However, some certain differences observed can be attributed to enhanced CO\(_2\) adsorption because of the strong interaction potential arising from the pore walls.

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