SANS Investigations of CO₂ Adsorption in Microporous Carbon

J. Bahadur¹, Y. B. Melnichenko^{1*}, L. He¹, C. I. Contescu², N.C. Gallego², J. R. Carmichael³

¹Biology and Soft Matter Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN
37831, USA

³Fusion & Materials for Nuclear Systems, Oak Ridge National Laboratory, Oak Ridge, TN
37831, USA

Abstract

The high pressure adsorption behavior of CO₂ at T=296 K in microporous carbon was investigated by small-angle neutron scattering (SANS) technique. A strong densification of CO₂ in micropores accompanied by non-monotonic adsorption-induced pore deformation was observed. The density of confined CO₂ increases rapidly with pressure and reaches the liquid – like density at 20 bar, which corresponds to the relative pressure of $P/P_{sat} \sim 0.3$. At $P > 20$ bar density of confined CO₂ increases slowly approaching a plateau at higher pressure. The size of micropores first increases with pressure, reaches a maximum at 20 bar, and then decreases with pressure. A complementary SANS experiment conducted on the same microporous carbon saturated with neutron-transparent and non-adsorbing inert gas argon shows no deformation of micropores at pressures up to ~ 200 bars. This result demonstrates that the observed deformation of micropores in CO₂ is an adsorption-induced phenomenon, caused by the solvation pressure - induced strain and strong densification of confined CO₂.

Keywords: Adsorption, CO₂, SANS, Sequestration

***Corresponding author:** Tel: +1 865 576 7746. Email: melnichenkoy@ornl.gov

1. Introduction

Porous carbons are widely used in many energy- and environmental-related applications [1]. In particular, high surface area and chemical stability makes them attractive as catalyst supports and efficient matrices for gas capture, separation, and storage [2, 3]. It has been established that microporosity plays an important role in gas adsorption of light molecules [4-8]. The fluids confined in such small pores exhibit properties significantly different from those of the corresponding bulk fluids at similar thermodynamic conditions. The presence of wall forces, and competing fluid–wall and fluid–fluid forces, can lead to interesting surface-induced effects. For example, if fluid-substrate attraction is sufficiently strong, micropore filling accompanied by enhanced densification of the fluid occurs at thermodynamic conditions markedly different from those of the corresponding bulk fluid. The density of the confined fluids often exceeds the bulk fluid density at the same temperature and pressure, as demonstrated by SANS and volumetric gas adsorption measurements [9,10].

First experimental evidences of the pore deformation in charcoal upon exposure to gases or vapors were documented as early as in 1927 [11]. More recently, deformation of carbons during the adsorption of different fluids has been investigated by Fomkin and co-workers [12–14] and a dilatometric study of the deformation of carbon xerogels has been conducted by Balzer and co-workers [15]. These studies concluded that dimensional modification of micropores in the adsorbents made the most significant contribution to the expansion and contraction of these materials [12-15].

Understanding the adsorption-induced deformation of the porous matrix remains one of the enduring problems in adsorption science [16–20]. The adsorption of fluid molecules leads to development of stress which is responsible for modification of the nano-mechanical properties of micropores. The origin of the stress is related to the packing of the fluid molecules in the micropores [21]. The magnitude of the stress depends on the pressure, fluid-pore wall interaction and pore size. The adsorption induced stress in the micropores is also known as solvation pressure [22]. Simulation studies [22, 23] have shown that in pores of a few times the diameter of the fluid molecules, adsorption-induced solvation pressure plays a decisive role. Depending on the relative contribution of adsorption and confinement effects, this stress may be either positive or negative leading to either swelling or contraction of the micropores. The adsorption stress caused by adsorbed molecules in micropores is significantly large, of the order of several GPa [24-27]. The extent of the pore deformation depends on the elastic modulus of the porous matrix. As the solvation pressure varies with the size of the pore, it may lead to highly inhomogeneous distribution of the elastic strain in the microscopic level for a sample with polydisperse pore size distribution [24-27].

It was recently demonstrated using small-angle X-ray scattering that ordered pores, e.g. in SBA-15, may be also deformed upon capillary condensation and formation of the liquid-gas interface [28-32]. We believe that the suggested explanation may be valid for liquids in relatively large nanopores, however for pores with size of the order of few diameters of fluid molecules, the macroscopic concepts based on the formation of menisci may not be applicable. *In-situ* Small-angle X-ray/Neutron scattering is an excellent technique to probe the density of the adsorbed fluid and pore morphology at different length scales [33-35].

The present work aims to understand the phase behavior of CO₂ adsorbed in the meso- and micropores of activated carbon as function of fluid pressure. The studies were conducted using *in-situ* SANS, which represents a noninvasive technique that can deliver information on the properties of confined fluids as a function of pore sizes [36,37]. In this study we utilize, for the first time, a new high pressure cell that was designed and built to facilitate the pressure dependent SANS measurements up to 1000 bar and 523 K. The density of confined CO₂ and adsorption-induced deformation of pores has been studied as a function of pressure.

2. Experimental

2.1 Materials and gas adsorption characterization

UMC is a microporous carbon made available by MeadWestvaco Corporation (Charleston, SC). It was obtained through phosphoric acid activation of wood followed by secondary activation with KOH [38]. The powder grains have irregular shapes with typical size of ~100 μm . Physical properties were characterized by gas adsorption of CO₂ at 273 K and N₂ at 77 K using a Quantachrome Autosorb 1 C instrument with ASiQwin 2.0 data processing software [39]. The CO₂ uptake measurements up to 20 bar have been carried out at room temperature (296 K) using a Hidden Isochema IGA-01 high pressure microbalance.

2.2 Small-angle neutron scattering

In-situ SANS measurements have been carried out at the General Purpose SANS instrument of the High Flux Isotope Reactor, at Oak Ridge National Laboratory (ORNL) [40] with a neutron wavelength of 4.72 Å and wavelength resolution $\Delta\lambda/\lambda \sim 0.13$. Two sample-to-detector distance was chosen to cover an extended range of scattering vectors $0.005 < Q < 1.0$ Å⁻¹, where $Q = \frac{4\pi\sin(\theta)}{\lambda}$, 2θ is the scattering angle. The measurement time at short and long

sample to detector distance was typically 5 min and 10 min, respectively. In our earlier studies [39,41,42] the maximum Q value that could be reached using high-pressure cells was limited to $0.65 \text{ \AA}^{-1}$ due to the cutoff angle of the cell which limited the size of the smallest pores to $\sim 10 - 15 \text{ \AA}$. In order to increase the accessible acceptance angle, a new "dome"-type cell was designed and commissioned, with maximum scattering angle of $\sim 180^\circ$. Cross-sectional and isometric views of the high pressure dome cell are shown in Fig. 1.

Figure 1 (A) cross-sectional view of the dome cell. Labels: (1) cell body, (2) hemispherical ("dome"-like) sapphire spacer, (3) sealing nut, (4) aluminum sample holder, (5) pressure adapters, (6) titanium sealing insert, (7) brass plate, (8) wire retainer, and (9) spring energized c-ring seal. (B) isometric view of the cell assembly.

Powder carbon samples were outgassed for ~ 5 hours at 300°C and loaded into a thin-wall aluminum container with 1.6 mm internal thickness, and subsequently mounted inside the high-pressure cell. The samples were studied under vacuum (pressure less than 10^{-3} mbar) to explore the texture and pore structure, and then carbon dioxide was injected to study its phase

behavior under confinement. The CO₂ pressure was varied, using a home built pressure setup, from vacuum to ~ 51.4 bar, and all measurements were conducted at room temperature (~296±1 K). The equilibration time was typically 5 minute after CO₂ was introduced in the sample. There is no significant pressure drop after 5 minutes of equilibrium time indicating short saturation time for the present pressure range. This is also supported by gravimetric adsorption measurements that showed equilibrium was reached in less than 5 minutes after each incremental pressure increase at room temperature. All data were corrected for instrumental background, transmission and detector efficiency.

To analyze the SANS data quantitatively, the scattering data needs to be put on absolute scale, which requires knowledge of the sample thickness. For bulk liquid samples the thickness is identical to the internal spacing between the windows of the sample holder. Thickness of bulk solids may be easily measured, however situation is more complicated when sample is prepared in the form of powders that don't completely fill the sample holder volume due to the availability of voids between the particles. In present case, powder sample is placed in aluminum sample holders for high-pressure cells with the internal thickness L (~1.6 mm). It is expected that in the case of powder the effective sample thickness L_{eff} will be less than the nominal thickness of the sample holder due to the presence of interparticle voids. The effective thickness L_{eff} of the powder sample in a container is related to its skeletal (ρ_{skel}), apparent (ρ_{app}), bulk (ρ_{bulk}) density and sample porosity V'_{pore} [cm³/g] as follows: $L_{eff} = L \frac{\rho_{bulk}}{\rho_{app}}$ where $\rho_{app} = (\rho_{skel}^{-1} + V'_{pore})^{-1}$. Bulk density ρ_{bulk} can be determined by weighing powder loaded sample holder with the known internal volume. The bulk density in present case is estimated to be 0.25 g/cm³. The sample porosity was measured using gas adsorption method [39]. The total sample pore volume V'_{pore} was found to be ~ 1.42 cm³/g [39]. The skeleton density was measured using the helium

pycnometry and its value was found to be $\sim 1.8 \text{ g/cm}^3$. The apparent density was estimated as 0.51 g/cm^3 using the expression above. Thus, the calculated effective thickness of the porous carbon powder sample was estimated as 0.78 mm. The corrected data was put on absolute scale (the cross section $I(Q)$ in units of cm^{-1}) using pre-calibrated secondary standards [43] and the effective thickness of the powder sample.

3. Results and Discussion

3.1 Volumetric gas adsorption

The specific surface area, calculated using Brunauer–Emmett–Teller (BET) equation, was found to be $2540 \text{ m}^2/\text{g}$. The pore surface area and pore volume from adsorption data using quenched surface DFT (QSDFT) analysis for pores are reported earlier [39]. All data were corrected for buoyancy using carbon skeleton density measured by Helium displacement. The CO_2 uptake mass (%) is reported as $\frac{\text{Weight of adsorbed } \text{CO}_2}{\text{weight of dry carbon}} \times 100$. The critical temperature and pressure of bulk CO_2 is 304 K and 73.8 bar. The bulk CO_2 below its critical temperature can be treated as vapor, and condenses at saturated vapor pressure P_{sat} . The saturated vapor pressure depends on the temperature. The adsorption and scattering experiment is performed at 296 K, the saturated vapor pressure P_{sat} is equals to 60.1 bar at this temperature. The CO_2 mass uptake as a function of pressure is shown in Fig. 2.

Figure 2 Excess CO₂ uptake in the UMC at various pressures at 296 K.

Uptake of CO₂ increases sharply at low pressure and tends towards a saturation value beyond relative pressure ~ 0.3 . The strong adsorption of CO₂ at lower pressures indicates presence of micropores in UMC with strong interaction with CO₂ molecules.

3.2 SANS analysis of dry UMC

The experimental SANS profile for the dry UMC carbon is shown in Fig. 3.

Figure 3 SANS profile of the dry UMC carbon specimen

The scattering in low Q range ($Q < 0.01 \text{ \AA}^{-1}$) follows a power law behavior; i.e., $I(Q) \sim Q^{-\alpha}$; the value of exponent α is ~ 3.5 . For a rough surface the scattering intensity follows power law behavior and exponent of the power law α varies in the range of 3 to 4. For an extremely rough surface $\alpha \sim 3$ and for a smooth surface $\alpha \sim 4$. The real space distance d is inversely related to the wave vector Q , i.e., $d = 2\pi/Q$. The minimum accessible Q value in present experiment is $0.00464 \text{ \AA}^{-1}$ which corresponds to the largest accessible length scale $\sim 1350 \text{ \AA}$ ($0.135 \text{ \mu m}$). The surface of the powder grains scatters in lowest Q regime. The scattering intensity in the intermediate Q -range is dominated by scattering from the mesopores. The scattering from micropores is manifested in the high- Q regime. We adopted the three length scale model to fit the SANS data. The scattering contributions from widely separated length scales may be simply added. The scattering intensity (neutron cross section per unit sample volume in units of cm^{-1}) from for such hierarchical system can be written as follows:

$$I(Q) = I_g(Q) + I_{meso}(Q) + I_{micro}(Q) + B \quad (1)$$

The first term describes surface scattering from the grains, the second and the third term describes the intensity of scattering from the mesopores and micropores, respectively and B represents the incoherent background. The expressions for three scattering contributions are elaborated below.

The first term describes surface scattering of power law nature from grains, i.e.,

$$I_g(Q) = C_g Q^{-\alpha} \quad (2)$$

The constant C_g is related to the specific surface area S/V of the grain-void interface and scattering contrast between grain and void. According to Porod, for surfaces that appear smooth on a distance scale $1/Q$, α is equal to 4 and $C_g = 2\pi(\Delta\rho^*)_g^2 \frac{S}{V}$ where $(\Delta\rho^*)_g = \rho_g^* - \rho_v^*$ is neutron scattering contrast between grain and void. Scattering length density (SLD) of the void ρ_v^* depends upon bulk CO₂ density and becomes zero for UMC under vacuum. SLD of the grain ρ_g^* depends on the porosity of the grains.

The SLD of the grains ρ_g^* can be expressed as below,

$$\rho_g^* = (1 - \phi)\rho_s^* + \phi\rho_p^* \quad (3)$$

where ϕ is the total pore volume fraction of the grains which includes mesopores and micropores, i.e., $\phi = \phi_{meso} + \phi_{micro}$ where ϕ_{meso} and ϕ_{micro} is the volume fraction of mesopore and micropores, respectively. ρ_s^* is the SLD of solid carbon skeleton of the grain and is equals to $6.0 \times 10^{10} \text{ cm}^{-2}$ assuming the physical density of solid carbon skeleton $\sim 1.8 \text{ g/cm}^3$. The total pore volume fraction ϕ for UMC is found to be 0.72. Thus SLD of UMC grain under vacuum is

estimated as $\sim 1.68 \times 10^{10} \text{ cm}^{-2}$. SLD of the pore ρ_p^* depends upon fluid density inside the pore. The fluid density inside mesopores and micropores may be different due to size dependent confinement effects. Thus ρ_p^* will be the average of SLD in mesopore and micropores, i.e., $\rho_p^* = (\phi_{\text{meso}}\rho_{\text{meso}}^* + \phi_{\text{micro}}\rho_{\text{micro}}^*)/\phi$. ρ_p^* will be zero for UMC under vacuum. Using eq. 3, the average neutron scattering contrast between the grain and the void can be written as,

$$(\Delta\rho^*)_g = (1 - \phi)\rho_s^* + \phi\rho_p^* - \rho_v^* \quad (4)$$

At sub-nanometer length scale, the shape of pores in most activated carbons is frequently regarded as slit-like. However, at larger length scales, the pore shape is no longer slitlike. Integrating pore shape, size polydispersity, and multi-length scales in the fitting will mitigate the reliability of the data fitting. Fitting the high-Q SANS data for cylindrical shape of micropores indicates that the average width and length of cylindrical micropores were approximately the same ($\sim 6 \text{ \AA}$). Moreover, we found that the shape of the pores is a not very sensitive parameter in the fitting of high Q SANS data, which might be due to nature of complex pore morphology and the low resolution nature of this technique. Hence, it is rational to assume spherical shape of the micropores for fitting purposes. The spherical pore morphology of the micropores was used previously for analysis of small angle scattering data [33].

The expression for the scattering intensity for polydisperse spherical pores can be written as follows [44]

$$I(Q) = N (\Delta\rho^*)^2 \int V^2(r)D(r) P(Q, r)dr \quad (5)$$

N is the number density of the pores, $(\Delta\rho^*)$ is the scattering contrast and $P(Q, r)$ is the spherical form factor and it can be expressed as,

$$P(Q, r) = 9 \left[\frac{\sin(Qr) - Qr \cos(Qr)}{(Qr)^3} \right]^2 \quad (6)$$

$D(r)$ is the lognormal pore size distribution and can be written as,

$$D(r) = \frac{1}{\sqrt{2\pi\sigma^2}r^2} \exp\left(-\frac{(\ln(r/r_0))^2}{2\sigma^2}\right) \quad (7)$$

where r_0 is the median size and σ is the polydispersity index of the distribution. The average pore size r_{av} may be estimated using the following relation $r_{av} = r_0 \exp\left(\sigma^2/2\right)$.

The scattering contrast for mesopores can be written as follows,

$$(\Delta\rho^*)_{\text{meso}} = \rho^{*'}_g - \rho^*_{\text{meso}} \quad (8)$$

where $\rho^{*'}_g$ is SLD of the grain excluding macropore and mesopores and ρ^*_{meso} is SLD of the fluid in the mesopores. The $\rho^{*'}_g$ depends on the microporosity in UMC and may be written as,

$$\rho^{*'}_g = (1 - \phi_{\text{micro}})\rho^*_s + \phi_{\text{micro}}\rho^*_{\text{micro}} \quad (9)$$

where ϕ_{micro} is the microporosity of the UMC.

Similarly, scattering contrast for micropores may be written as follows,

$$(\Delta\rho^*)_{\text{micro}} = \rho^*_s - \rho^*_{\text{micro}} \quad (10)$$

where ρ^*_s and ρ^*_{micro} represents SLD of solid skeleton carbon and fluid in micropore, respectively. Both ρ^*_{meso} and ρ^*_{micro} will be zero for UMC under vacuum.

The fitting of the model (eq. 1) to the scattering profile of UMC under vacuum is shown in the Fig. 3. The scattering contributions from different length scales are also shown. The finite

incoherent background B in the dry UMC carbon is related to the presence of functional groups (such as phenols, carboxylic acids) containing hydrogen atoms. Chemical analysis of UMC is consistent with a $C_{28.2}HO$ elemental formula. Temperature-programmed desorption coupled with mass spectroscopy (TPD-MS) (not shown here) indicates that oxygen is present in majority in $>C=O$ groups that release CO above 600 °C; minor amounts of carboxyl groups that release CO_2 at 300 – 600 °C were also found. Weakly bonded physisorbed water, which is released below 150 °C, was removed during outgassing before SANS experiments. However, hydrogen was not removed, and was the main cause of the incoherent background.

The pore size distribution for mesopores and micropores is obtained by fitting of the SANS data using eq. 1. It is important to recall that the polydisperse sphere model is considered for mesopore/micropore scattering contribution in eq. 1.

Figure 4 Micropore and mesopore radius distribution of the dry UMC carbon specimen

The average size (diameter) of the micropores and mesopores is estimated as $\sim 5.0 \text{ \AA}$ and $18 \text{ \AA}$, respectively.

3.3 SANS analysis of UMC with CO₂

The evolution of the scattering intensity at different CO₂ pressure is shown in Fig. 5.

Figure 5 SANS profiles of UMC as a function of CO₂ pressure. The error bar in the scattering data is less than the size of the symbols. SANS profiles are shown for few representative pressures only for sake of clarity. Solid lines represent model fits to the data.

It is evident from Fig. 5 that there are crossovers between scattering profiles at both low and high-Q. In general the contrast variation does not involve the crossover of scattering profiles.

However in present case, injection of CO₂ in UMC modifies the scattering contrast at larger and smaller length scales in opposite way this gives rise to crossover of scattering profile. Moreover, the functionality of the scattering profiles at high Q also varies with pressure leading to crossover at high Q. As may be seen in Fig. 5, on a log-log scale, scattering intensity in the low-Q regime ($Q < 0.006 \text{ \AA}^{-1}$) increases in parallel fashion as a function of the fluid pressure/density. This indicates that this increase is due to the rising scattering contrast between the granules and voids and is not associated with any structural changes of the grains. At the same time, the increase in the scattering intensity in the intermediate-Q range ($0.006 \text{ \AA}^{-1} < Q < 0.10 \text{ \AA}^{-1}$) and high-Q regime ($Q > 0.10 \text{ \AA}^{-1}$) is non-parallel and Q-dependent. The scattering profiles for all relative pressures have been fitted using three length scale model described by eq. 1.

The scattering contributions from grain, mesopore and micropores have been extracted at each pressure using model fitting. Figs. 6, 7 and 8 show the scattering contributions from grains, mesopores and micropores for some representative pressures, respectively.

Figure 6 *The evolution of grain scattering at different CO_2 pressure. Scattering profiles are shown for few representative pressures for sake of clarity.*

Figure 7 The evolution of mesopore scattering at different CO_2 pressure. Scattering profiles are shown for few representative pressures for sake of clarity.

Figure 8 *The evolution of micropore scattering at different CO₂ pressure. Scattering profiles are shown for few representative pressures for sake of clarity.*

It is evident from Figs. 6 and 7 that shape of the scattering profiles from grains and mesopores does not change with pressure whereas its scale modifies. It is evident from Fig. 8 that both the functionality and scale of the scattering profile from micropores varies with pressure.

The grain contrast $(\Delta\rho^*)_g$ has been estimated by fitting and is shown with mass uptake of CO₂ measured by adsorption technique in Fig. 9. It is to be noted that the constant prefactor C_g in eq. 2 depends on grain contrast, specific surface area, and surface fractal dimension [45]. The fractal dimension and specific surface area of the grains remains independent of CO₂ pressure and hence variation in C_g can be attributed only due to variation in the grain contrast at different pressure. The absolute value of the grain contrast for UMC under vacuum is known and hence

the grain contrast for each pressure is estimated using normalization of C_g values at each pressure and is represented in absolute unit in Fig. 9.

Figure 9 Grain contrast $(\Delta\rho^*)_g$ and mass uptake as function of pressure

Fig. 9 demonstrates close similarity of the variation of grain contrast and the mass uptake as a function of pressure. Further, the upper pressure limit of the technique used for measurements of excess gravimetric uptake is 20 bar whereas the neutron scattering measurements could measure the mass uptake at higher pressure. Thus low-Q scattering behavior in present case provides an estimation of mass uptake in a wider pressure range. The variation of scattering contrast of grain may be understood based on eq. 4. SLD of void ρ_v^* is equal to the SLD of bulk CO_2 which increases with pressure. The scattering contrast between grain and voids should have been decreased with pressure if the SLD of pores and voids is same at each pressure. This will happen if there is no densification of fluid in pores. The observed opposite trend, i.e., increase of contrast between grains and voids implies that the average SLD of the grains increases much faster than

the SLD of the bulk fluid in the voids. Grain contrast starts to decrease at $P/P_{\text{sat}} \sim 0.85$ because of substantial increase in density of bulk CO_2 at high pressure. From eq. 3, it is evident that the SLD of the grains depends upon the SLD of the fluid confined in the pores inside the grains. We will show later that strong densification of CO_2 occurs in the micropores at low pressures leading to the rapid increase in the average SLD of the grain.

The contrast factor for mesopores $(\Delta\rho^*)_{\text{meso}}$ has also been estimated by fitting the experimental SANS profiles and is depicted in Fig. 10. The contrast factor of mesopore increases up to $P/P_{\text{sat}} \sim 0.3$ due to densification of carbon matrix as result of anomalously large adsorption of CO_2 in micropores (eq. 9). The density of fluid inside mesopores remains small below $P/P_{\text{sat}} \sim 0.3$. As pressure increases beyond $P/P_{\text{sat}} \sim 0.3$, the density of CO_2 in the mesopores increases sharply leading to decrease in contrast factor.

Figure 10 Mesopore contrast $(\Delta\rho^*)_{\text{meso}}$ as function of pressure

The contrast factor for micropores $(\Delta\rho^*)_{\text{micro}}$ has been estimated from fitting the experimental data and is depicted in Fig. 11.

Figure 11 Micropore contrast $(\Delta\rho^*)_{\text{micro}}$ as function of pressure

It is evident that scattering contrast in micropores decreases very sharply at lower pressure indicating a strong densification of the adsorbed CO₂ in micropores. Beyond $P/P_{\text{sat}} \sim 0.1$ the slope of contrast variation gradually decreases, pointing out to saturation of CO₂ adsorption in micropores at P/P_{sat} in the range of 0.3-0.4. At pressures beyond $P/P_{\text{sat}} \sim 0.5$ the contrast factor increases a little due to slight decrease in the density of adsorbed CO₂. At relatively high pressures the filling of the wider micropores (similar to the small mesopores) occurs with reduced adsorbed density. This results into slight reduction in the averaged density of adsorbed CO₂ leading to increase in the contrast factor.

Figure 12 The schematic of UMC carbon (a) dry (b) at low CO_2 pressure (c) at high CO_2 pressure.

The length scale- and pressure-dependent contrast variations in UMC during adsorption of CO_2 is illustrated in Fig. 12. The UMC grains consist of micropores, and mesopores embedded in the solid carbon skeleton (Fig. 12a). At low CO_2 pressures (Fig. 12b), the micropores are filled with high density adsorbed CO_2 whereas low density bulk CO_2 is present in the voids between the grains. Thus the average SLD of the grains and hence the contrast factor for grain scattering increases. At low pressures the density of confined fluid in the mesopores is comparable to that of bulk CO_2 . The mesopores are embedded in the matrix having micropores filled with dense adsorbed CO_2 . Thus the contrast for mesopores also increases due to increase in the density of the matrix at lower pressures. The density of the adsorbed CO_2 in micropores gets saturated at lower pressure and it does not increase afterwards whereas the density of confined CO_2 in mesopores keeps on increasing at higher pressure (Fig. 12c) leading to decrease in the mesopore contrast. Moreover, the filling of the mesopores leads to further increase in the grain contrast. In present model it is assumed that density of adsorbed CO_2 is the same in all micropores at a given pressure. We did not consider the size dependent density variation within the micropores at a given pressure in order to avoid complexity in the analysis. This is a first order approximation

and is valid due to finite range of pore sizes. A similar assumption is made for adsorption in the mesopores.

The pore size distributions of micropores at different pressures estimated by the fitting of the SANS data using eq. 1 are shown in Fig. 13. The average pore size as a function of pressure is shown in Fig. 14. We observe a non-monotonic trend in the pore size with pressure. The pore radius increases by 50 % with pressure up to ~14 bar and then starts to decrease at higher pressure.

Figure 13 Pore size distribution of micropores at different pressure. Distributions are shown for few representative pressures for sake of clarity.

The density of CO₂ confined in the micropores can be estimated by calculating Porod Invariant γ from the scattering intensity at different pressures:

$$\gamma = \int_0^\infty Q^2 I(Q) dQ = 2\pi^2 (\rho_s - \rho_{micro})^2 \phi_s (1 - \phi_s) \quad (11)$$

The Porod invariant does not depend on the structure of the two phases but only on the volume fractions and contrast between the two phases. The SLD of the micropores depends on the density of adsorbed CO₂. The scattering length density of the adsorbed fluid in the pore is related to the Porod invariant as follows:

$$\rho_u = \left(1 - \sqrt{\frac{\gamma}{\gamma_{vac}}}\right) \rho_s \quad (12)$$

The density of CO₂ confined in the micropores as estimated by eq. 12 and the average radius of micropores as a function of pressure are shown in Fig. 14. This figure also shows the variation of the density of bulk CO₂ as a function of pressure. Also shown for comparison are the solid CO₂ density at ~1.01 bar and T=194.5 K and the liquid CO₂ density at the saturation pressure P_{sat}(=60.1 bar) corresponding to T= 296 K.

Figure 14 The variation of the average diameter of micropore (▲), density of confined CO₂ (■) and bulk CO₂ (○) in UMC as function of pressure.

The density of the CO₂ in the micropore increases rapidly at small pressures and remains significantly higher than the density of bulk CO₂ at the same thermodynamic conditions. The density of confined fluid at $P/P_{\text{sat}} \sim 0.3$ is equal to the liquid density. The density of adsorbed CO₂ continues to increase exceeding the liquid density at higher pressure. The maximum density of confined CO₂ is found to be approximately $\sim 1.0 \text{ g/cm}^3$ which is in between liquid and solid CO₂ density (0.7 g/cm^3 and 1.5 g/cm^3 , respectively). As may be seen in Fig. 14, the average size of micropores initially increases quickly with pressure and decreases slightly at pressures higher than $P/P_{\text{sat}} \sim 0.3$. This indicates that the nature of pore deformation depends on the density of the adsorbed fluid. The effective internal pressure of CO₂ confined in micropores was estimated from the density-pressure relationship using the non-ideal equation of state for CO₂ [46]. The estimated internal pressure P_{int} in micropores at each bulk CO₂ pressure P_{ext} is shown in Table 1. It is well known that density of bulk subcritical CO₂ is a discontinuous function of pressure. At the critical pressure the density of the fluid diverges. In the equation of state of bulk CO₂ at 296 K [46] there exists a forbidden density range between 0.2 to 0.7 g/cm^3 corresponding to the transition between subcritical to supercritical conditions. Based on SANS measurements, the density of confined CO₂ varies continuously between 0.14 and 0.92 g/cm^3 . No density discontinuities were observed for the density of CO₂ confined in micropores, and no attempts were made to calculate the internal pressure of confined CO₂ having density values in the forbidden range.

Table 1 Bulk density, micropore size, confined density in micropores and estimated internal pressure in the micropores are depicted as a function of CO₂ pressure.

P _{ext} (bar)	Bulk density (g/cm ³)	Pore size (Å)	Confined CO ₂ density (g/cm ³)	P _{int} (bar)
0	0	4.89	0	0
0.48	0.0008	5.79	0.1402	51.5
1.03	0.0018	5.95	0.1722	56.4
2.96	0.0054	6.39	0.2529	-
6.27	0.0116	6.85	0.4576	-
7.79	0.0145	6.99	0.5279	-
9.23	0.0173	7.07	0.5975	-
14.54	0.0282	7.29	0.7217	-
20.34	0.0410	7.19	0.9295	209.9
30.06	0.0665	6.68	1.0420	499.7
35.51	0.0807	6.17	0.9584	264.1
51.43	0.1421	5.44	0.9248	200.5

The results in Table 1 demonstrate that P_{int} in the micropores increases between 45 and 500 bar when P_{ext} varies from 0.5 to 30 bar. The internal pressure due to confined CO₂ in micropores is much higher than the bulk pressure P_{ext}, especially at low external pressures. A similar result was reported for the internal pressure of hydrogen confined in carbon nanopores [42].

The densification factor has been estimated by taking the ratio of the confined and bulk fluid densities. The excess density of confined fluid in micropores has been calculated as the difference between the densities of confined and bulk CO₂. The variation of both parameters with pressure is shown in Fig. 15. It is evident that densification factor is ~ 150 at the lowest pressure. Its value decreases sharply up to $P/P_{\text{sat}} \sim 0.05$ and then reduces relatively slowly at higher pressure. The excess density of CO₂ in micropore increases up to $P/P_{\text{sat}} \sim 0.5$ then decreases slightly at higher pressure.

Figure 15 The variation of the densification factor (▲) and excess density (■) of confined CO₂ in micropores as a function of pressure. The density of bulk CO₂ (○) is also shown.

3.4 SANS analysis of UMC under high pressure argon

In principle, there are two possible mechanisms that could cause the observed deformation (initial expansion followed by a contraction) of micropores, namely adsorption of CO₂ or hydrostatic pressure. To clarify the reason for the micropore deformation, a similar SANS experiment was performed with UMC exposed to increasing pressures of argon, which is a non-adsorbing gas transparent to neutrons. The measurements were conducted over the range of pressures $1 < P < 200$ bar. Even at the highest pressure, the SLD of argon is about 60 times lower than the SLD of carbon, which makes its contribution to the contrast factor and scattering intensity negligibly small in the studied range of pressures. Fig. 16 shows that the SANS profiles remain unchanged at all pressures implying that there is no pore deformation caused by the hydrostatic pressure. This leads to the conclusion that the observed deformation of micropores in the CO₂ experiment is caused by strong adsorption effects.

Figure 16 *The SANS profiles of UMC under various Ar pressure*

3.5 Origin of deformation of micropores

The SANS experiment with argon demonstrates that the deformation of the micropores can be attributed to the adsorption induced solvation stress. The average diameter of micropores is estimated to be 4.9 Å. The typical diameter of CO₂ molecule is ~3.7 Å [47]. It is evident that only one layer of CO₂ molecules can fit in these pores. The fluid-solid interaction is quite strong due to overlapping interaction potentials of opposite pore walls in this size range. The strong fluid-solid interaction causes high densification of CO₂ molecules and large solvation pressure [48-50]. The pore walls behave as elastic solid and respond to solvation induced stress leading to increase in the size of the pores. As pressure increases, CO₂ molecules try to enter the pores leading to higher pore filling degree and densification. The solvation pressure depends on the pore width and fluid pressure and it increases with increasing fluid pressure and decreases with increasing pore width [51,52]. At pressure $P/P_{\text{sat}} \sim 0.3$ the pore width exceeds twice the diameter of the CO₂ molecules. This leads to decrease in the solvation pressure and corresponding reduction of the solvation-induced stress. The non-monotonic variation of the size of micropores is closely linked to the non-monotonic behavior of solvation pressure. It is also apparent from Table 1 that internal pressure in the micropores P_{int} is quite high as compared to the bulk CO₂ pressure P_{ext} due to strong solid-fluid interactions. The deformation of micropores may also be caused by this difference in pressure. We can define the compression factor as the ratio of P_{int} and P_{ext} . Interestingly, the compression factor shows non-monotonic behavior with pressure P_{ext} which is qualitatively similar to the variation of micropores size. In order to understand the deformation of micropores precisely one should take into account all the relevant factors such as solid-fluid interactions, fluid-fluid interactions, solvation pressure related to the packing of the fluid molecule in pores, and the large adsorption induced internal pressure. In order to validate

the reversibility of the pore deformation scattering profile is recorded for UMC under vacuum after end of pressure cycle. The SANS profiles of UMC under vacuum before and after pressure cycle is compared in Fig. 17. It is evident from the figure that scattering profiles looks identical within the experimental error. This proves that deformation of micropores is reversible in nature.

Figure 17 *The SANS profiles of the UMC sample under vacuum before and after the pressure cycle.*

4. Conclusions

The adsorption of subcritical CO₂ in UMC porous carbon as a function of pressure has been studied using in situ SANS. The scattering profiles have been interpreted using three length scale model. The scattering contrast at three different length scales shows strikingly different variation with pressure. The intensity of scattering in the low-Q domain follows closely the gravimetric adsorption behavior of CO₂. Strong densification of CO₂ in micropores is accompanied by the pore deformation. The pore size increases from ~5.0 Å to 7 Å as relative

pressure reaches $P/P_{\text{sat}} \sim 0.3$ and decreases at higher pressures. The SANS experiments on UMC under high pressure of Ar do not reveal any structural changes. This indicates that the micropore deformation is caused by CO_2 adsorption. The internal pressure corresponding to the dense CO_2 in micropores exceeds much the external applied CO_2 pressure. It is conjectured that the non-monotonic pore deformation is due to adsorption-induced solvation pressure, strong fluid-solid interaction and large internal pressure corresponding to the dense fluid.

Acknowledgements:

The research at Oak Ridge National Laboratory's High Flux Isotope Reactor was sponsored by the Laboratory Directed Research and Development Program and the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. This research was supported in part by the ORNL Postdoctoral Research Associates Program, administered jointly by the ORNL and the Oak Ridge Institute for Science and Education. CIC and NCG acknowledge support from the Materials Science and Engineering Division, Office of Basic Energy Sciences, U.S. Department of Energy

References:

- [1] Azar C, Lindgren K, Larson E, Möllersten K. Carbon capture and storage from fossil fuels and biomass—Costs and potential role in stabilizing the atmosphere. *Clim Change* 2006; 74: 47–79.
- [2] Yong Z, Mata VG, Rodrigues AE. Adsorption of carbon dioxide on chemically modified high surface area carbon-based adsorbents at high temperature. *Adsorption* 2001; 7: 41–50.

- [3] Sevilla M, Valle-Vigón P, Fuertes AB. N-doped polypyrrole-based porous carbons for CO₂ capture. *Adv Funct Mater* 2011; 21: 2781–2787.
- [4] Yang Z, Xia Y, Mokaya R. Enhanced hydrogen storage capacity of high surface area zeolite-like carbon materials. *J Am Chem Soc* 2007; 129(6) : 1673–1679.
- [5] Vix-Guterl C, Frackowiak E, Jurewicz K, Friebe M, Parmentier J, Bèguin F. Electrochemical energy storage in ordered porous carbon materials. *Carbon* 2005; 43 (6):1293–1302.
- [6] Cracknell RF, Gordon P, Gubbins KE. Influence of pore geometry on the design of microporous materials for methane Storage. *J Phys Chem* 1993; 97:494–499.
- [7] Lozano-Castelló D, Cazorla-Amorós D, Linares-Solano A, Hall PJ, Gascon D, Galan C. In situ small angle neutron scattering study of CD₄ adsorption under pressure in activated carbons. *Carbon* 2001; 39 (9):1343–1354.
- [8] Chen XS, Mcenaney B, Mays TJ, Alcaniz-Monge J, Cazorla-Amoros D, Linares-Solano A. Theoretical and experimental studies of methane adsorption on microporous carbons. *Carbon* 1997; 35 (9): 1251–1258.
- [9] Melnichenko YB, Wignall GD, Cole DR, Frielinghaus H. Adsorption of supercritical CO₂ in aerogels as studied by small-angle neutron scattering and neutron transmission techniques. *J Chem Phys* 2006; 124 (20): 204711.
- [10] Tsao C, Li M, Zhang Y, Leao JB, Chiang W, Chung T, Tzeng Y, Yu M, Chen SH. Probing the room temperature spatial distribution of hydrogen in nanoporous carbon by use of small-angle neutron scattering. *J Phys Chem C* 2010; 114(47):19895-19900.

- [11] Meehan FT. The expansion of charcoal on sorption of carbon dioxide. *Proc R Soc London A* 1927; 115 (770): 199–207.
- [12] Fomkin AA, Regent NI, Sinitsyn VA. Adsorption deformation in the microporous carbon adsorbent-benzene system and porous structure of adsorbents. *Russ Chem Bull* 2000; 49 (6): 1012–1016.
- [13] Yakovlev VY, Fomkin AA, Tvardovski AV, Sinitsyn VA, Pulin AL. Adsorption-stimulated deformation of microporous carbon adsorbent. *Russ Chem Bull* 2003; 52 (2): 354–358.
- [14] Shkolin AV, Fomkin AA. Deformation of AUK microporous carbon adsorbent induced by methane adsorption. *Colloid J* 2009; 71 (1): 119–124.
- [15] Balzer C, Wildhage T, Braxmeier S, Reichenauer G, Olivier JP. Deformation of porous carbons upon adsorption. *Langmuir* 2011; 27 (6): 2553–2560.
- [16] Tvardovskiy AV. Sorbent deformation. Elsevier Ltd.: Oxford; 2007.
- [17] Bangham DH, Fakhoury N. The expansion of charcoal accompanying sorption of gases and vapours. *Nature* 1928; 122: 681-682.
- [18] Bangham DH. The Gibbs adsorption equation and adsorption on solids. *Trans Faraday Soc* 1937; 33: 805-811.
- [19] Haines RS, McIntosh R. Length changes of activated carbon rods caused by adsorption of vapors. *J Chem Phys* 1947; 15: 28–38.
- [20] Maggs, FAP. The adsorption-swelling of several carbonaceous solids. *Trans Faraday Soc* 1946; 42: B284-B288.

- [21] Günther G, Schoen M. Sorption strain as a packing phenomenon. *Phys Chem Chem Phys* 2009; 11: 9082–9092.
- [22] Kowalczyk P, Ciach A, Neimark AV. Adsorption-induced deformation of microporous carbons: Pore size distribution effect. *Langmuir* 2008; 24(13): 6603-6608
- [23] Yang K, Lu X, Lin Y, Neimark AV. Deformation of Coal Induced by Methane Adsorption at Geological Conditions. *Energy Fuels* 2010; 24: 5955–5964.
- [24] Striolo A, Chialvo AA, Cummings PT, Gubbins KE. Water adsorption in carbon-slit nanopores. *Langmuir* 2003; 19(20): 8583-8591.
- [25] Sizov VV, Piotrovskaya EM, Brodskaya EN. Influence of a surface microheterogeneity on the disjoining pressure of adsorbed Lennard–Jones fluid. computer simulation. *Colloid J.* 2003; 65(6): 772-777.
- [26] Ustinov EA, Do DD. Effect of adsorption deformation on thermodynamic characteristics of a fluid in slit pores at sub-critical conditions. *Carbon* 2006; 44 (13): 2652-2663.
- [27] Balbuena PB, Berry D, Gubbins KE. Solvation pressures for simple fluids in micropores. *J Phys Chem* 1993; 97:937-943.
- [28] Zickler G, Jähnert S, Wagermeier W, Funari S, Findenegg G, Paris O. Physisorbed films in periodic mesoporous silica studied by in situ synchrotron small-angle diffraction. *Phys Rev B* 2006; 73: 184109.
- [29] Scherer GW. Dilatation of porous glass. *J Am Ceram Soc*, 1986; 69(6): 473-480.

- [30] Dolino G, Bellet D, Faivre C. Adsorption strains in porous silicon. *Phys Rev B* 1996; 54: 17919.
- [31] Herman T, Day J, Beamish J. Deformation of silica aerogel during fluid adsorption. *Phys Rev B* 2006; 73: 094127.
- [32] Grosman A, Ortega C. Influence of elastic deformation of porous materials in adsorption-desorption process: A thermodynamic approach. *Phys Rev B* 2008; 78: 085433.
- [33] Nguyen TX, Bhatia SK. Characterization of accessible and inaccessible pores in microporous carbons by a combination of adsorption and small angle neutron scattering. *Carbon* 2012; 50: 3045-3054.
- [34] Mileeva Z, Ross DK, Wilkinson D, King SM, Ryan TA, Sharrock H. The use of small angle neutron scattering with contrast matching and variable adsorbate partial pressures in the study of porosity in activated carbons. *Carbon* 2012; 50: 5062–5075
- [35] Favvas EP, Stefanopoulos KL, Papageorgiou SK, Mitropoulos AC. In situ small angle X-ray scattering and benzene adsorption on polymer-based carbon hollow fiber membranes. *Adsorption* 2013; 19: 225–233.
- [36] Ciccariello S., Melnichenko YB, He L. Phase behavior of carbon dioxide confined in silica aerogel in the vicinity of the bulk critical point. *J Phys Chem C* 2012; 116 (21): 11848–11848.
- [37] Melnichenko YB , Mayama H, Cheng G, Blach T. Monitoring phase behavior of sub- and supercritical CO₂ confined in porous fractal silica with 85% porosity. *Langmuir*, 2010; 26 (9): 6374–6379

- [38] Baker FS, Beckler RK, Miller JR, Yan ZQ, Highly microporous carbons and process of manufacture. U.S. patent 5965483, 1999.
- [39] He L, Melnichenko YB, Gallego NC, Contescu CI, Guo J, Bahadur J. Investigation of morphology and hydrogen adsorption capacity of disordered carbons Carbon 2014; 80: 82–90.
- [40] Wignall GD, Littrell KC, Heller WT, Melnichenko YB, Bailey KM, Lynn GW, et al. The 40 m general purpose small-angle neutron scattering instrument at Oak Ridge National Laboratory. J Appl Crystallogr 2012; 45:990–8.
- [41] He L, Melnichenko YB, Mastalerz M, Sakurovs R, Radlinski AP, Blach T. Pore Accessibility by Methane and Carbon Dioxide in Coal as Determined by Neutron Scattering, Energy Fuels 2012; 26: 1975–1983.
- [42] Gallego NC, He L, Saha D, Contescu CI, Melnichenko YB. Hydrogen confinement in carbon nanopores: extreme densification at ambient temperature. J Am Chem Soc 2011; 133 (35):13794–13797.
- [43] Wignall GD, Bates FS. Absolute calibration of small-angle neutron-scattering data. J Appl Crystallogr 1987;20:28–40.
- [44] Glatter O, Kratky O. Small-angle X-ray scattering. Academic Press; 1982
- [45] Radlinski AP. Reviews in Mineralogy & Geochemistry 2006; 63: 363-397.
- [46] Span R, Wagner W. A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa. J Phys Chem Ref Data 1996; 25(6): 1509-1596.

- [47] Hirschfelder JO, Curtiss CF, Bird RB. Molecular Theory of Gases and Liquids. New York: Wiley;1954.
- [48] Stefanopoulos KL, Steriotis TA,. Katsaros FK, Kanellopoulos NK, Hannon AC, Ramsay JDF. Structural characterization of subcritical carbon dioxide confined in nanoporous carbon by in situ neutron diffraction. J Phys Conf Ser 2012; 340; 012049.
- [49] Steriotis TA, Stefanopoulos KL, Mitropoulos AC, Kanellopoulos NK, Hoser A, Hofmann M. Structural studies of supercritical carbon dioxide in confined space. Appl Phys A 2002; 74: S1333.
- [50] Steriotis TA, Stefanopoulos KL, Kanellopoulos NK, Mitropoulos AC, Hoser A. The structure of adsorbed CO₂ in carbon nanopores: a neutron diffraction study, Coll and Surfact A 2004; 241: 239.
- [51] Günther G, Prass J, Paris O, Schoen M. Novel insights into nanopore deformation caused by capillary condensation. Phys Rev Lett 2008;101:086104.
- [52] Günther G, Schoen M. Sorption strains and their consequences for capillary condensation in nanoconfinement. Mol Simul 2009; 35: 138-150.