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Neutron Scattering from Porous Materials and Confined Fluids: Applications to CO₂ Sequestration and Oil Recovery

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Abstract In the current study we briefly review the advantages of utilising elastic neutron scattering techniques to reveal the structure of porous materials and pore-confined fluids. Furthermore, we highlight the benefits of utilising *in situ* CO₂ injection and neutron scattering in model porous systems as well as in sedimentary rocks to explore the pore morphology, the pore accessibility and the structural properties of pore-confined CO₂. This information is important for the design of optimal CO₂ sequestration as well as gas and oil recovery projects.

Keywords neutron scattering, porous materials, confined fluids, CO₂ sequestration, oil recovery

INTRODUCTION

Neutron scattering techniques constitute a powerful tool to probe non-destructively the structure and the dynamics of materials. Elastic neutron scattering involves processes in which there is no energy loss between the incident and the scattered neutrons. Neutron diffraction, total neutron scattering, small-angle neutron scattering (SANS) and ultra-small-angle neutron scattering (USANS) are powerful tools to probe and reveal the structural properties of porous media at length scales from interatomic distances up to a few micrometers. In addition, when neutron scattering is combined with *in situ* gas sorption, valuable information can be also obtained about the structure, the phase behaviour and the location of the pore-confined fluid.

An important advantage of these methods is that neutrons are sensitive to probe the structure of materials that contain light atoms (such as H, D, Li, C, N, O). The reason is that light elements may be poorly located in x-ray diffraction experiments, especially when high-Z elements are also present. Another advantage of neutron diffraction is that the Bragg peaks have similar intensities over the whole pattern while in x-ray diffraction patterns the intensity of Bragg reflections decreases with the increasing 2θ angle.

Another unique advantage of neutrons relies on the fact that they are scattered differently by the various isotopes of an element (such as H and D). In case of carrying out (U)SANS experiments on porous materials, by filling the pores using an appropriate mixture of hydrogenous and deuterated solvents (such as H₂O/D₂O) the scattering of the solid matrix becomes equal to that of the mixture, contrast matching is then attained and the scattering signal is eliminated. By applying contrast matching (U)SANS one can gain valuable information not only about the accessible (open) and inaccessible (closed) porosity but also about the sorption mechanism of fluids.

In the following we will briefly review the benefits of utilising elastic neutron scattering technique to probe the structural properties of porous materials and pore-confined fluids. These methods are very useful particularly for materials with complex pore architecture and closed porosity like sedimentary rocks.

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EXPERIMENTAL SET-UP

One more advantage of neutrons versus x-rays is their high penetration capability because they have no charge and they interact with atomic nuclei with relatively weak interactions. This means that neutron experiments provide information about the bulk of the sample rather than its surface. As a result, most neutron applications are non-destructive. For x-rays, typical sample thickness varies from 0.01 to 1 mm, whereas neutron samples range from 0.5 to 5 mm. The neutron penetration capability makes then easier to utilise advanced sample environment such as gas handling equipment, cryostats, furnaces and high-pressure sample cells for monitoring *in situ* various processes at the nanoscale such as sorption on porous media [1] (Fig. 1).

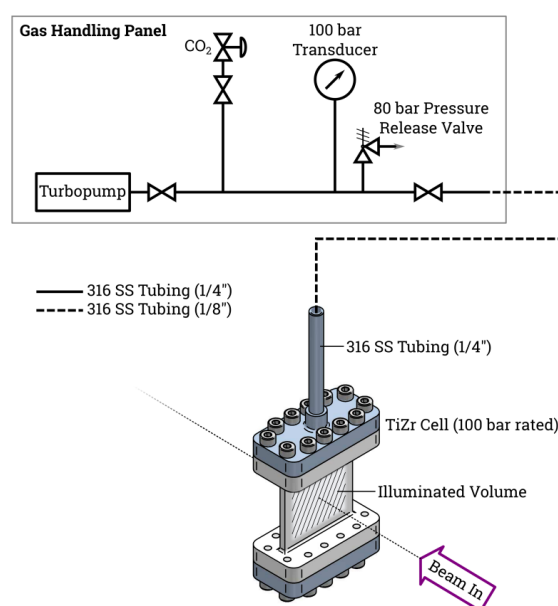


Fig. 1. Typical experimental set-up for carrying out *in situ* gas sorption and neutron scattering experiments in porous materials. Schematic from Ref. 1.

METHODOLOGY

Neutron diffraction

Neutron diffraction is a powerful tool for probing the structure at interatomic distances of crystalline porous materials that contain light atoms. As an example, metal-organic frameworks (MOFs) have recently attracted a lot of interest; they are crystalline porous materials composed of metal-based building units coordinated to organic bridging ligands to form a three-dimensional network with uniform pore system including channels and cages. Neutron diffraction offers unique chances for unfolding key features of their complex structure. In addition, by combining gas sorption and neutron diffraction valuable information can be obtained both about the precise locations of the guest gas molecules (especially H₂ and D₂) within the pore cavities and their interactions with the crystalline framework [2].

Total neutron scattering

The atomic arrangement in real crystals exhibits always deviations from the ideal periodicity due to thermal vibrations, dislocations etc. This type of “weak disorder” gives rise to diffuse scattering

resulting in a reduction in the Bragg scattering. When only Bragg scattering is taken into account, for example by Rietveld refinement, the diffuse scattering is simply assumed as background. Disordered materials however, such as liquids and porous solids, exhibit short-range or limited-range crystalline structure. This means that the correlations between the disordered structural features are contained in the diffuse scattering. The structural information can therefore be revealed only by the measurement of the total scattering (Bragg scattering and diffuse scattering). In principle, there are no major differences between a neutron total scattering instrument and a neutron powder diffractometer. They are both used to measure the scattering intensity as a function of the momentum transfer (or the scattering vector), Q . However for total scattering measurements, the instrument should have the capability to collect data over a very large Q range with sufficient resolution (see for example NIMROD instrument, [3]).

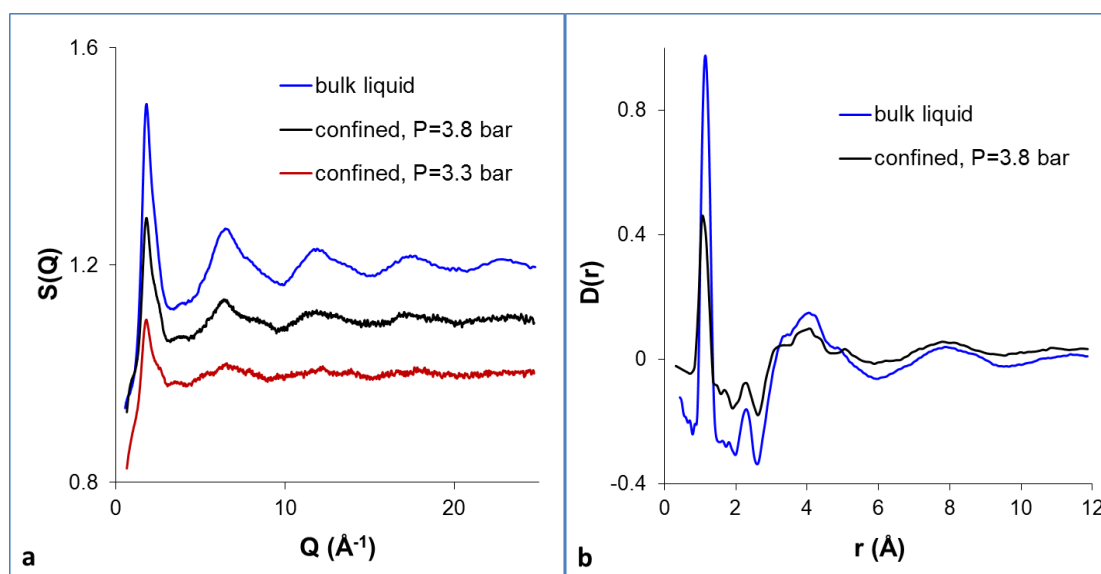


Fig. 2. (a) The total scattering structure factor at 214 K for confined CO_2 into SBA-15 at 3.3 and 3.8 bar and for bulk liquid (230 K, 12 bar). The structure factors have shifted by 0.1 for clarity; (b) The differential correlation function at 214 K for confined CO_2 at 3.8 bar and for bulk liquid. Data from Ref. 6.

Confined fluids have attracted a lot of attention during the last years because their importance for various applications such as catalysis, gas storage, chromatography, oil recovery, CO_2 sequestration and many others. From the theoretical point of view, when fluids are confined in nanoscale pores, the combination of solid-fluid interactions and finite volume can significantly alter their structural and dynamic properties and strongly influence their phase behavior. These structural differences can be revealed by combining *in situ* sorption and neutron total scattering in model porous systems (see for example, [4-7]), (Fig. 2). In addition, various processes within the pores can be also monitored at real time, such as the kinetics of the toluene hydrogenation reactions within the pores of a Pt/MCM-41 catalyst [8]. Further, it was observed that during cooling down CO_2 confined in SBA-15 below its bulk triple point the CO_2 molecules, instead of freezing, escaped from the pores [6]. Importantly, that combination of neutron scattering experimental data and atomistic Monte Carlo simulations can provide detailed information concerning the accurate positions of the confined fluids within the pores [9-10].

Small-angle and ultra-small-angle neutron scattering (SANS-USANS)

Complementary to neutron total scattering that measures interatomic distances, SANS probes the structures at larger length scales (or small Q -values), varying from 1 nm to a few hundred nanometers while USANS probes lengths up to a few micrometers (about 10 μm). (U)SANS is an essential tool for the structural characterization of the porous materials by providing information about the geometry and topology of the pores, the interface texture (smooth or rough), the total porosity, the pore size distribution and the specific surface area.

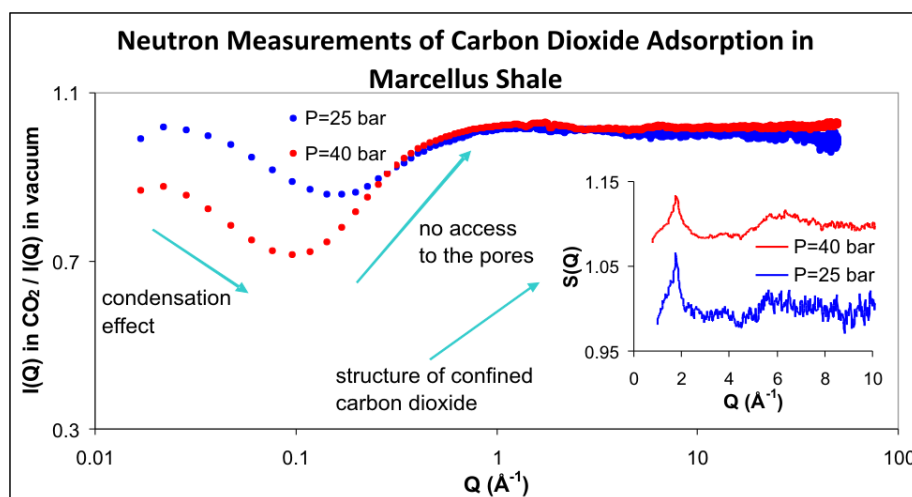


Fig. 3. Pore accessibility to CO_2 and the total scattering structure factor for pore-confined CO_2 into a Marcellus shale sample. Data from Ref. 1.

One of the main advantages of the technique is the utilisation of contrast matching SANS. Contrast matching SANS is a very powerful method for a direct investigation and evaluation of the closed porosity in porous media. In practice, the technique is applied by performing SANS on dry samples, where the total scattering comes from all the available pores, including both accessible (open) and inaccessible (closed) pores. As a next step, the accessible pores are saturated with a contrast matching mixture of a hydrogenous and deuterated solvent (for example $\text{H}_2\text{O}/\text{D}_2\text{O}$) and, thus, scattering from open porosity is eliminated. Consequently, the residual scattering signal yields information only about closed porosity in the materials [11-12]. Melnichenko and coworkers suggested an alternative method of achieving contrast matching in porous media by using non-adsorbing or weakly adsorbing supercritical fluids or gases, such as carbon dioxide CO_2 or deuterated methane, CD_4 (instead of CH_4 , for minimising the incoherent background scattering from hydrogen). In a similar way, by measuring the scattering patterns as a function of fluid pressure, when the contrast matching pressure or the zero average contrast (ZAC) is reached, the residual scattering simply indicates the presence of pores inaccessible to CO_2 or CD_4 [13-17].

Combination of gas sorption and contrast matching SANS in porous materials has also been proved to be an essential tool for elucidating the adsorption mechanism and for highlighting also the structural details of the porous matrix [18-20]. Neutrons provide the unique possibility to obtain structural characteristics, hardly accessible by other analytical techniques. In particular, they allow studying all stages of the fluid adsorption in porous media such as micropore filling, formation of adsorbed layers, and capillary condensation in mesopores.

In general, the complex pore architecture of sedimentary rocks (such as coal, shales, sandstones, carbonates and others) is a scientifically fascinating subject of major practical importance. Combined gas sorption, mercury porosimetry and neutron scattering techniques have been extensively utilised as multi-scale methods for probing the rock microstructure. It has been discovered that sedimentary rocks display the most extensive fractal behavior observed in nature, with self-similarity expanding over at least three orders of magnitude in the length scale [21-22]. In addition, the microstructure, the evolution of porosity and the pore accessibility to fluids play a crucial role in many geological processes including CO₂ sequestration and oil recovery. For instance, in the case of shale, by *in situ* injection of pressurised CO₂ and total neutron scattering and SANS measurements it was concluded that oil recovery would be unlikely to displace petroleum from the smaller pores because they are effectively closed to CO₂ (Fig. 3). Importantly, this finding also suggests that during anthropogenic CO₂ sequestration the studied Marcellus shale specimens would be probably unavailable for storage [1,23].

CONCLUSIONS

In conclusion, elastic neutron scattering techniques are essential tools for probing structural details of porous materials and pore-confined fluids. In particular, revealing the complex pore architecture of sedimentary rocks, the pore accessibility to CO₂ and the structure of confined CO₂ are of great importance because the microstructure and evolution of porosity plays a critical role in many geological processes including CO₂ sequestration and oil recovery. It would be also challenging to further utilise the potentiality of neutrons to monitor *in situ* structural changes, phase transitions and molecular interactions in the nanopores during various processes such as sorption, flow, catalytic reactions, enhanced oil recovery and by *in operando* charging-discharging batteries.

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