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Research Note

# Overall investigation of the behavior of water/ice in almost and partially filled nanopores of SBA-15 silica by neutron diffraction technique

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## KEYWORDS

Neutron diffraction;  
Confined geometry;  
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**Abstract.** A neutron diffraction technique is used to study the structural characterization of water/ice in mesoporous SBA-15 silica with 86Å nanopore diameter. Different filling factors of the silica pores were considered over a wide temperature range. Neutron diffraction data for the almost-filled case, with a filling factor of 0.95, which undergoes a temperature change of 300-100K, shows a main asymmetric triplet peak  $1.74\text{Å}^{-1}$ . Using five symmetric functions, we found an excellent fit with the whole range of data sets for the triplet. Interestingly, each of these functions is directly linked to the position of the different ice components and shows a systematic variation of peak parameters. As a complementary experiment, data analysis of the partially-filled cases, with filling factors of 0.6 (300-130 K) and 0.4 (300-100 K), show characteristics that are markedly different from those of the filling factor 0.95. The nucleation temperature for all cases is reduced and different ice structures, along with their temporal order, have been detected for confined water. Further investigations confirm that for different filling factors, there are different amounts of hexagonal, cubic and disordered ice components. Surprisingly, data analysis proved the reversibility of the whole nucleation process, although the formation/melting of the ice in the main body of the pore showed the expected hysteresis.

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## 1. Introduction

Increasing interest is being shown towards the use of partially-filled mesoporous samples, as they may be used to investigate the behaviour of a thin water layer [ $<20\text{Å}$ ] near an interface. Much of this development has focused strongly on the properties of water in a biosciences context. Studies of water/ice in confined geometry have emphasized the complex behaviour of confined states as a function of temperature and filling-

factor [1-6]. Considering over-filled, almost filled, and partially filled samples clearly shows how the filling factor ( $f$ ) plays a key role, as important as temperature. In this paper, we present the results of an overall investigation into confined water/ice behaviour with different filling factors of pores in a wide range of temperatures.

## 2. Experimental measurements

The measurements were made on a D20 diffractometer at the ILL, with an incident wave length of  $2.400 \pm 0.005\text{Å}$ . The sample was prepared by adding a calcu-

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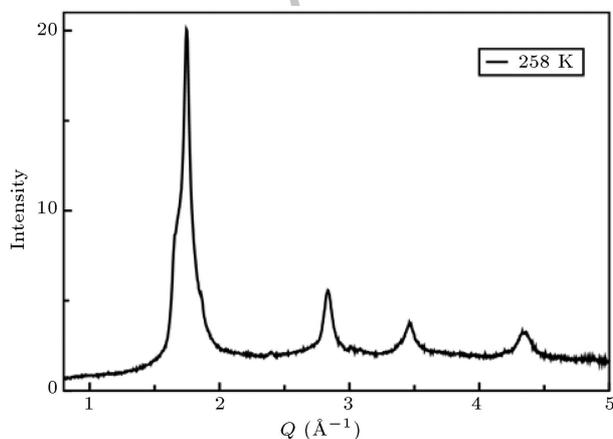
lated quantity of  $D_2O$  to the SBA-15 sample for each of the filling factors, and leaving it to equilibrate for at least three hours. Measurements were made with a constant temperature ramp in both cooling and heating modes. The usual data processing was conducted to convert the recorded data into an intensity pattern, as a function of the scattering vector,  $Q$ , at various temperature intervals. Using two component analysis procedures, we tried to find different ice components formed inside these nanopores. First, we performed a parameter fitting routine using symmetric sech functions to extract the variation of peak intensities and shapes with temperature, and relate each peak to an ice component. Using the second method, neutron diffraction cryoporometry, we confirm these conclusions and emphasize the role of so called 'plastic ice' in the phase conversion process for 260-200 K.

### 3. Results and discussion

Distribution of water in the nanopore volume will change by reducing the value of the filling-factor,  $f$ , and  $f$  is known to have a significant effect on the nucleation event. In all filling factors, peaks in the region of 1.5 to  $2.0 \text{ \AA}^{-1}$  are of prime interest and the intensity profiles have been shown in Figures 1-3.

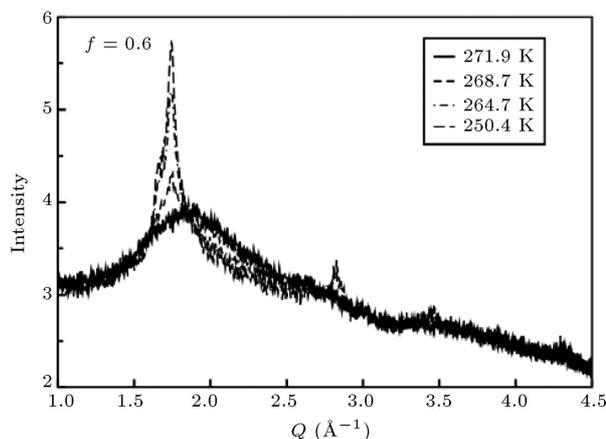
A parameter fitting routine using five symmetric sech functions has been used for  $f = 0.95$  and  $f = 0.6$  and an excellent fit was found in the main region of our data (Figures 4 and 5).

It was found that the three sharp peaks (peaks 1, 3 and 5) corresponding to the Bragg peaks for ice-I could be well fitted by this method, and showed the systematic variation of the peak position,  $Q_0$ , and the width and intensity of the peaks. The broader peaks, 2 and 4, which are required to define the disordered components of the profile for the case of  $f = 0.95$ , exhibited a modified behaviour, particularly for peak 2, for  $f = 0.6$ . For the case of  $f = 0.95$ , the

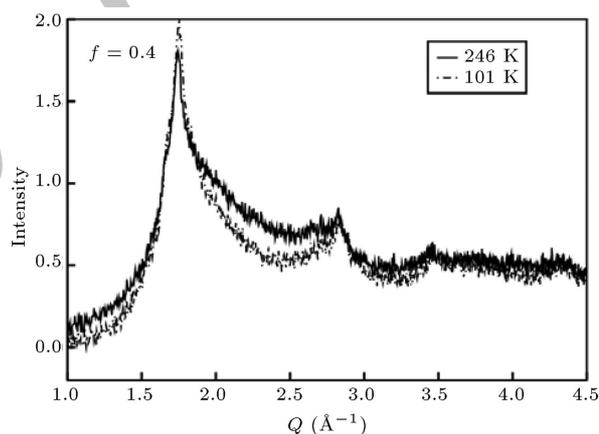


**Figure 1.** Neutron diffraction pattern of water/ice with  $f = 0.95$  at 258 K.

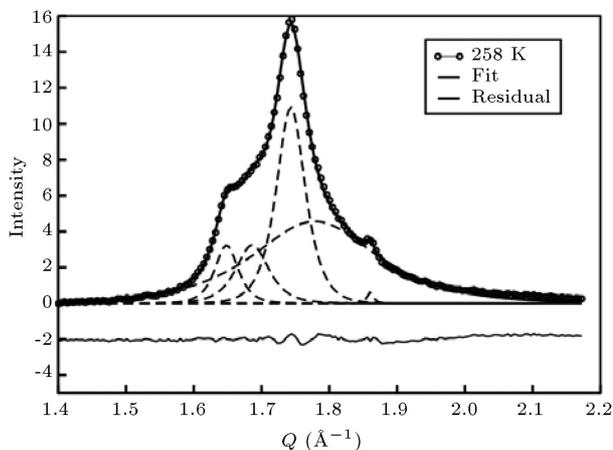
behaviour of peaks 1 and 5 suggest that the amount of hexagonal ice is much less than cubic ice, which has one peak at the center of the triplet. For the case of  $f = 0.6$ , the behaviour of the first peak indicates that the initial stage of nucleation involves the formation



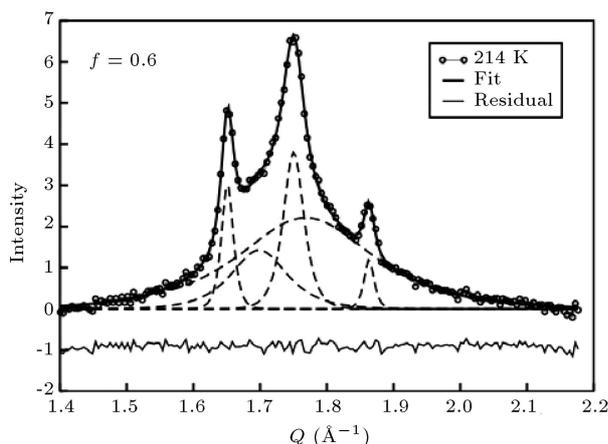
**Figure 2.** Neutron diffraction pattern of water/ice with  $f = 0.6$  at 271.9 K, 268 K, 264.7 K and 250.4 K.



**Figure 3.** Neutron diffraction pattern of water/ice with  $f = 0.4$  at 246 K and 101 K.



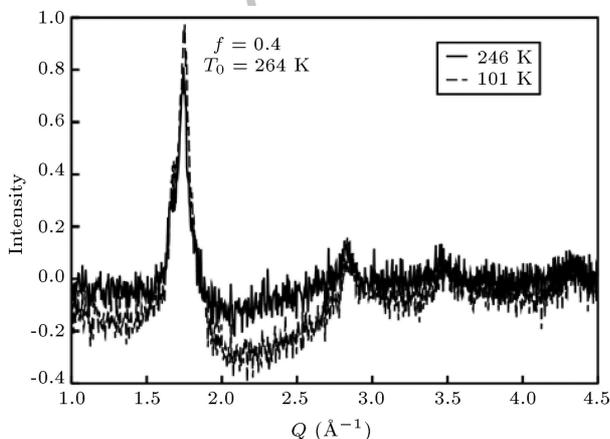
**Figure 4.** The fitted profile using five symmetric peak functions for  $f = 0.95$  at temperature 258 K.



**Figure 5.** The fitted profile using five symmetric peak functions for  $f = 0.6$  at temperature 214 K.

of a defective form of cubic ice. Also, the hexagonal ice only starts to grow at a lower temperature and the amount of hexagonal ice formed inside the nanopores is much more than the amount formed in the case of  $f = 0.95$ . Surprisingly, this effect is reversible, so that the hexagonal ice seems to melt before the defective cubic ice, as the temperature is increased. The nucleation process shows the initial development of a distinct but broad central peak before either of the two outside peaks of the triplet. However, the shoulder at low  $Q$ -values indicates that there is a precursor to the [100] peak. These observations suggest that proto-crystals grow preferentially in the [002] direction, in the initial stages of nucleation, but the broad peak indicates that they are either disordered or of small size. This behavior again emphasizes the complexity of the phase relations and transformations occurring in the water/ice mixture.

For the case of  $f = 0.4$ , the ice peaks are less easily distinguished from the broad pattern of amorphous ice and there is an almost complete disappearance of the outer components of the Bragg triplet (Figure 6). The

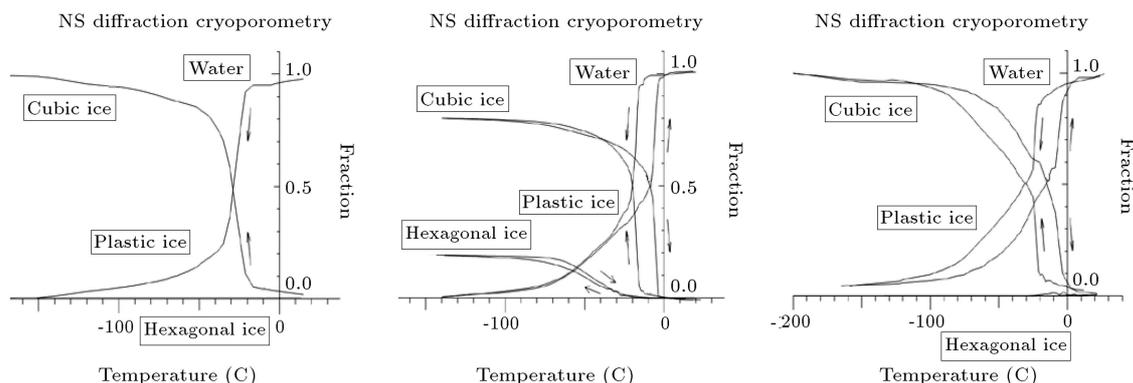


**Figure 6.** The difference function for  $f = 0.4$  at 246 K and 101 K, using a reference temperature,  $T_0$  of 264 K.

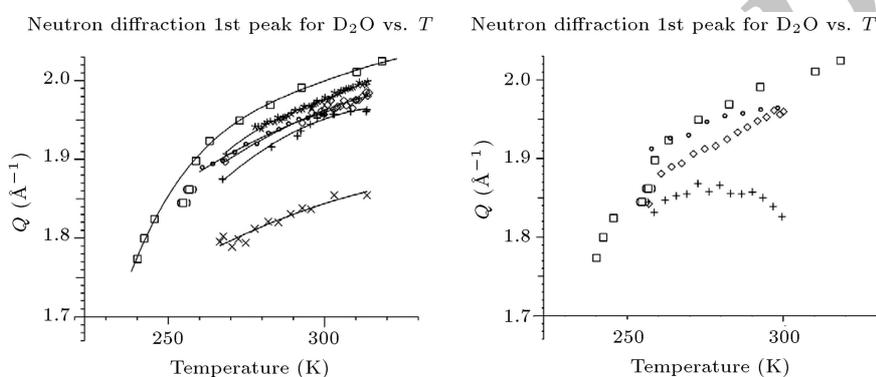
broad disordered peak plays a much more dominant role in the profile, making it difficult to distinguish the crystalline component. In this situation, it becomes desirable to remove this general scattering in order to obtain a satisfactory pattern for the growth of the crystalline component by subtracting this pattern from the lower temperature measurements to give a temperature difference function. This process clearly indicates the growth of the defective ice-Ic phase and the complete absence of any ice-Ih characteristics. An alternative way of presenting the phase changes with temperature is to use neutron diffraction cryoporometry, NDC [1], which emphasizes the phase relationships rather than the parameter variations required to fit the individual profiles. In this procedure, a template is used for each of the different forms of water/ice present in the diffraction pattern, namely hexagonal ice, cubic ice, and a disordered pattern that relates to an amorphous solid phase. Each of the measured diffraction profiles is then decomposed into a fraction of these three components, producing a representation of the phases as a function of temperature.

The results for the three filling-factors of 0.95, 0.6 and 0.4 are shown in Figure 7. As can be seen, for the different filling factors, there are differing quantities of hexagonal ice, cubic ice and the disordered component. The NMR work [2] suggests that this disordered component is not a liquid as it has a reduced translation, characteristic of a solid, but retains significant rotation. We have chosen to describe it as ‘plastic ice’ by analogy with organic plastic crystals that have similar dynamical features.

For  $f = 0.95$ , as shown in Figure 7, the water first super-cools to about  $-20^\circ\text{C}$  and then partially nucleates with the formation of cubic ice. The diffuse scattering component, represented as plastic ice, initially consists of about 25 - 30% of the ice in the nanopores. If it is assumed that the plastic ice forms preferentially at the silica interface [3-6], this would represent a layer of plastic ice about 6 to 8 Å thick at the wall of these 86 Å diameter nanopores. NMR relaxation measurements indicate that the interface dynamics can be up to a factor of ten times faster than in bulk brittle ice at the same temperature [7]. The fraction of plastic ice continues to decrease with temperature down to about 120 K, increasingly converting to crystalline cubic ice (brittle ice in NMR terms). These changes are believed to represent a reduction in the disorder produced in the ice by the presence of the silica interface, and that this induced disorder extends a shorter distance into the ice at lower temperatures. Negligible amounts of hexagonal ice are seen in these fully-filled nanopores ( $\sim 1\%$ ); this may be because there is little in the way of a liquid to vapor interface within which hexagonal ice can form. The pattern for  $f = 0.6$ ,



**Figure 7.** Neutron Diffraction Cryoporometry (NDC) graph showing the variation of component phases for cooling water/ice in a SBA-15 silica, from left to right,  $f = 0.95, 0.6, 0.4$ .



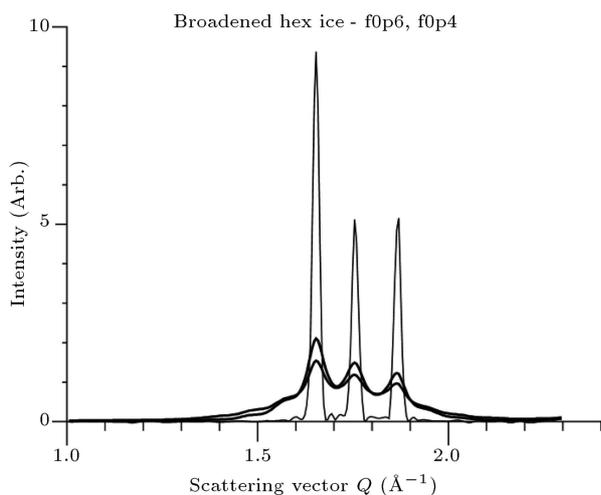
**Figure 8.** Comparative plots of  $Q_0(T)$  for various studies of bulk and confined water. Squares, for bulk water, diamonds, for SBA-15  $f = 0.95$ , plus signs for  $f = 0.6$  and hollow spheres for  $f = 0.4$ .

has a similar general behavior for the formation of cubic ice, except that less cubic ice is formed, as there is now a very significant fraction of hexagonal ice forming at lower temperatures. The plastic ice represents about 50% of the ice in the nanopores, on initial freezing. However, because  $f = 0.6$ , there is now only 60% as much ice in the nanopores; this still represents about a 7Å thick layer of plastic ice at the silica interface. At lower temperatures, the plastic ice converts to both cubic ice (about 80%) at 150 K and hexagonal ice (just under 20%), with one or two percent of plastic ice remaining. The conversion of the plastic ice to crystalline ice occurs continuously over an extended temperature range in the 150-260 K range. These ratios are consistent with the plastic ice at the silica interface converting to cubic ice, and the plastic ice at the vapor interface converting to hexagonal ice. There is increased hysteresis for the hexagonal ice in the 240 K to 260 K region. NMR relaxation data indicate that the dynamics of the plastic ice at the vapor interface can be up to a factor of ten times faster than at the silica interface [2]. The pattern for  $f = 0.4$ , has more statistical variation and follows a similar sequence, but, in this case, the final pattern at low temperatures is dominated by cubic ice and shows no evidence for the presence of any hexagonal ice. The plastic ice

component again shows a continuous change over the 150-260 K range. The  $f = 0.4$  filling corresponds to a surface layer of less than 10Å thickness in 86Å diameter pores. Thus, it would appear that the tendency to form cubic ice near a silica interface over this distance dominates any tendency to form hexagonal ice at an air/vapor interface. Comparative plots of  $Q_0(T)$  for various studies of bulk and confined water are shown in Figure 8. A comparison of measured scattering by bulk hexagonal ice, with calculated broadened scattering, for  $f = 0.6$  and  $f = 0.4$ , is illustrated in Figure 9, which shows increased broadening by reducing filling factor  $f$  for three studied cases. It is not a good idea to put all three measured neutron diffraction data on the same plot for comparison, since the process of fitting is different for these cases, although it is possible to put all the raw data on the same plot.

#### 4. Conclusions

The study of water/ice confined in partially filled nanopores of SBA-15 silica showed that the nucleation process is totally reversible, with interesting features. Different amounts/structures of ice were found compared to the bulk water, depending on the filling factors



**Figure 9.** Comparison of measured scattering by bulk hexagonal ice with calculated broadened scattering for  $f = 0.6$  and  $f = 0.4$ , showing increased broadening with reducing filling factor  $f$ .

of nanopores. The effect of pore size is still under investigation.

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#### Biographies

**Jamileh Seyed-Yazdi** obtained her BS degree in Physics from Ferdowsi University of Mashhad, Iran, her MS degree from Shiraz University, Iran, and her PhD degree in Condensed Matter Physics from Iran University of Science and Technology. She has undertaken neutron scattering experiments and MD simulation at the University of Kent, Canterbury, UK, and from La Sapienza University of Rome, and Virginia Commonwealth University, USA. She is currently Assistant Professor of Physics at Vali-e-Asr University of Rafsanjan, Iran. Her present research interests include graphene and other 2D electronic systems.

**John. C. Dore** is Emeritus Professor in the School of Physical Sciences at the University of Kent, Canterbury, UK. He has been interested in the study of disordered materials, such as liquids and glasses for over forty years using neutron and x-ray diffraction methods. He has a number of international collaborations and is currently interested in unusual states of water, either in confined geometry or in a doubly-metastable (i.e. negative temperature and pressure) state. A separate investigation is centred on carbon nanotubes and other carbon materials.

**J. Beau W. Webber** performs academic and commercial materials-science research into nano- to meso-science, studying the structure, dynamics and phases of liquids and their solids (and also gas hydrates) in confined geometry and at and near surfaces. This knowledge is then further directed into research into nano- to micro-volumetric metrology. Dr. Webber employs the experimental techniques of NMR, NS, SANS, QENS, WAXS, SAXS, DSC, and gas adsorption. The results from these measurements are interpreted by modelling analyses, and ab-initio QM molecular dynamics and other simulation techniques (CASTEP, EPR) to understand the physics of dynamical and structural processes and transformations. Previous conclusions include the observation of ice near interfaces in a dynamical state of rotational motion, with implications for the macroscopic study of ice and

snow-packs in the environment, and the evolution of water/ice in meteorites. Results from the study of gas hydrates in pores have significance with respect to global warming. Current work includes studies of the porosity of sandstone, shale and carbonate rocks as applied to oil recovery and gas extraction/sequestration, and the study of carbonaceous materials, such as

biochar, for CO<sub>2</sub> sequestration and soil amendment. Other current work includes studies on catalysts for a major multinational company, and a cooperative project with a major European research centre on clays. Dr. Webber's research has led him to develop novel NMR instrumentation, work currently supported by an €1.188m FP7 grant.

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