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# Dynamics at Surfaces : Probing the Dynamics of Polar and A-Polar Liquids at Silica and Vapour Surfaces

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**Abstract.** Recent studies by Nuclear Magnetic Resonance and Neutron Scattering of the dynamics and phase-fractions of water/ice systems in templated porous silicas (SBA-15) indicate that what was believed to be a non-frozen surface water layer is actually plastic ice, the quantity varying (continuously and reversibly) with temperature, and converting to a brittle (mainly cubic) ice at lower temperatures.

Current research relates to the study the dynamics of polar water/ice and a-polar organics at both solid and vapour interfaces. The polar results are significant for water/ice systems in the environment, where snow-packs, glaciers and icebergs are common examples of water/ice systems with extensive air/vapour interfaces.

This research also points the way forward for wide-range cryoporometric metrology in 'difficult' systems such as high iron content clays and rocks, as well as aged concrete. Results are presented for cryoporometric measurements on meteorite samples with a significant metallic content, exhibiting  $T_2^*$  relaxation times down to 2.5ms.

**Keywords:** confined geometry, phase-change, Gibbs-Thomson, neutron scattering, neutron diffraction, plastic ice, NMR, NMR relaxation, cryoporometry, DSC, thermoporosimetry, porous silica, meteorite, porosity

**PACS:** 64.60.-i, 81.07.-b, 61.12.Ld, 61.18.Fs, 03.75.Hh, 05.70.Fh, 64.60.Qb, 64.70.Dv, 68.03.Cd, 68.08.-p, 82.56.Na, 82.56.Ub, 61.43.Gt

## INTRODUCTION

This study was initiated following a neutron diffraction cryoporometric (NDC) analysis [1] of an extensive set of neutron diffraction measurements on D<sub>2</sub>O water/ice systems in SBA-15 and MCM silicas (cylindrical pores) [2, 3, 4], using the high-performance D20 diffractometer at ILL in Grenoble.

This data led to a set of NMR relaxation (NMR-R) measurements being performed on overfilled H<sub>2</sub>O water/ice systems in templated SBA-15; preliminary results were reported at MRPM8 in Bologna [5] and a more detailed analysis elsewhere [6]. This work has now been further extended and new measurements have been made on partially filled systems that have ice-vapour interfaces as well as ice-silica interfaces.

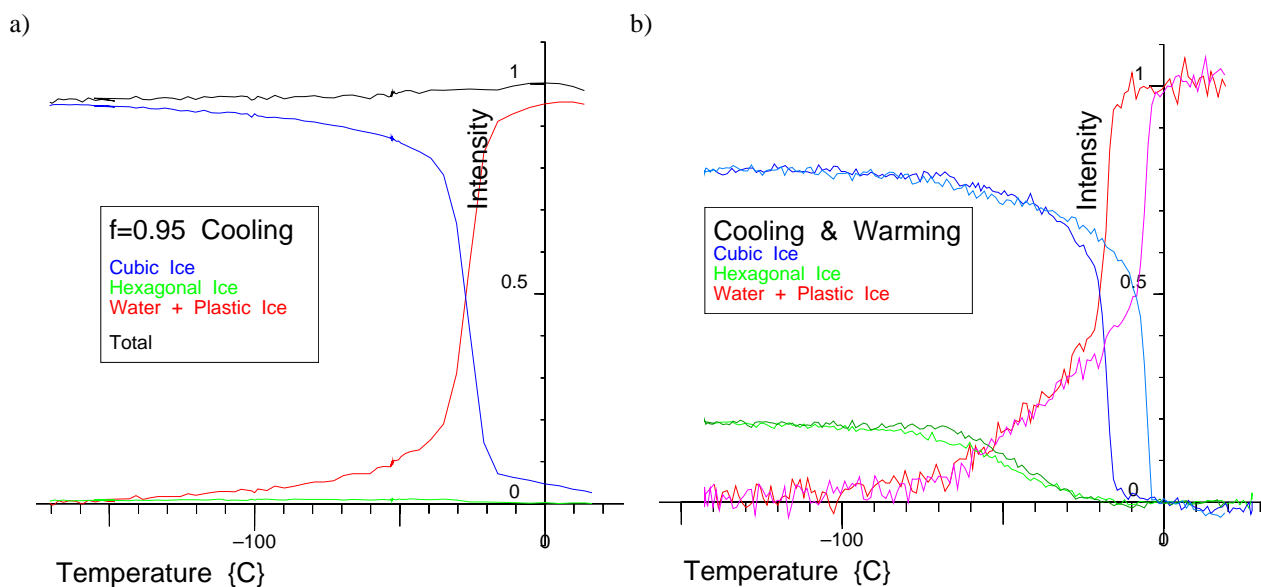
## POLAR LIQUIDS: FULLY-FILLED PORES: PLASTIC ICE AT THE ICE-SILICA INTERFACE

### Structure: Neutron Diffraction Cryoporometry study

The NDC technique presents plots of the quantities of each of the water/ice phases in the system being studied, as amplitude plots, in a similar manner to NMR cryoporometry (NMR-C) [7], which in turn is a development of the gas adsorption and differential scanning calorimetry (DSC) thermoporosimetry techniques.

The recent paper describing the NDC technique [1] concluded with the statement that the technique needed further development so as to return normalised amplitudes. It is believed that a reasonable approach to this normalisation has now been developed.

Results have been presented elsewhere for the overfilled water/ice system (i.e. the water/ice system fully fills the pores, with excess outside the grains,  $f=1.31$ ). The bulk water outside the pores can be seen to be freezing to predominately hexagonal ice, but the water in the pores can be seen freezing to mainly cubic ice, at a temperature lowered by the Gibbs-Thomson effect [7, 1].



**FIGURE 1.** Normalised Neutron Diffraction Cryoporometry graphs of  $D_2O$  water / ice fractions in SBA-15 templated silica. a) Nearly filled,  $f=0.95$ , b) partially filled,  $f=0.61$ .

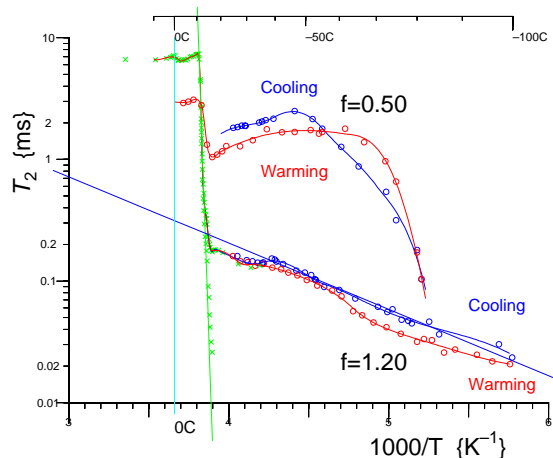
Figure 1a shows a normalised graph for the phase fractions for the SBA-15 pores nearly filled with  $D_2O$  ( $f=0.95$ ). In this graph the total of the displayed quantities for each of the three phases in the sample, water, cubic ice and hexagonal ice, at any particular temperature, sum to unity. A very significant feature of this graph is that nearly all the water in the pores converts to cubic ice, with only 1% hexagonal ice. It has been known for some time that the water in pores less than about 30 nm in diameter tends to form cubic ice, but these fractional plots are very enlightening - this data will be discussed further in the section on partial filling.

A particular feature of these graphs is the extended tail of a disordered component (best matched by the water template), that extends down to around -100 C. The dynamics of this component was then investigated by NMR relaxation.

#### Dynamics: NMR Relaxation study

NMR  $T_1$  and  $T_2$  measurements were made on an over-filled sample ( $f=1.20$ ), and, below the main freezing event in the pores, showed a two component signal, with one component being brittle ice with a  $T_2$  of around 10  $\mu s$ . The other component had a  $T_2$  that showed a plateau of around 100 to 200  $\mu s$ , becoming more brittle-ice like at around -80 C, see figure 2. The amplitude of this component also decreased progressively and reversible at low temperatures. This plateau in  $T_2$  is characteristic of plastic crystals, and is due to the rotational motion averaging the effective average positions of the protons to the molecular centres.

This leads to the conclusion that rather than being a measurement from a water layer, this was actually probably an observation of ice in state of predominantly rotational motion - "plastic ice" - this is discussed in more detail elsewhere : [2, 6]. While there is as yet no direct observational evidence, a working hypothesis has been that this is a layer of modified ice at the ice-silica interface; this hypothesis is discussed further in the next section.



**FIGURE 2.** NMR  $T_2$  relaxation data for  $H_2O$  plastic ice in SBA-15 templated silica. for  $f=1.20$  and  $f=0.50$ .

## **POLAR LIQUIDS: PARTIALLY-FILLED PORES: PLASTIC ICE AT ICE-SILICA AND ICE-VAPOUR INTERFACES**

A hypothesis that has been generated to understand both the fully-filled and partially filled pore NDC results, is that plastic ice forms at both the ice-silica and the ice-vapour interfaces, and that as the temperature is lowered, the plastic ice at the ice-silica interface converts to cubic ice, whilst the plastic-ice at the ice-vapour interface converts to hexagonal ice - this hypothesis is now evaluated with the measured results :

### **Structure: Neutron Diffraction Cryoporometry study**

A NDC analysis of neutron scattering measurements performed on partially filled SBA-15 pores ( $f=0.61$ ), figure 1b, shows that, on cooling, initially cubic ice and plastic-ice forms, but then as the temperature is lowered, the plastic ice converts in approximately equal quantities to cubic ice and hexagonal ice (slightly less hexagonal ice, as would be expected for the smaller interfacial area), the layers being up to about 3 Å thick. The maximum amount of hexagonal ice in the pore seems to be about 15% of the total pore volume.

Thus the small amount of hexagonal ice forming from the plastic ice, in the  $f=0.95$  study, can be understood as the presence of a small fraction of the pores containing air, giving rise to plastic ice at the vapour surface, then converting to hexagonal ice. The slightly larger amount of plastic ice converting to hexagonal ice in the  $f=1.31$  study must by this hypothesis be understood as indicating that this sample was insufficiently well equilibrated, and that a small percentage of pores were not fully filled by the time the experiment was performed (there were only a limited number of sample cans, and time pressure to keep taking results).

### **Dynamics: NMR Relaxation study**

The overlaid data for the  $T_2$  times for an NMR-R study of partially filled SBA-15,  $f=0.50$ , shows that the relaxation in this component is substantially slower (figure 2). Again there is a plateau in the relaxation time, further supporting the conclusion that this is an observation of plastic ice. These results are a superposition of the relaxation times from the plastic ice at the ice-silica and ice-vapour interfaces, and the initial rise as the temperature is lowered may reflect a changing in the ratio of the two components.

## **A-POLAR LIQUIDS: FULLY FILLED PORES**

There is an interest in applying the technique of NMR-C to the study of rocks, clays and cements - in some of these environments there is low iron and paramagnetic content, and standard NMR-C techniques using water work well using  $2\tau$  echo sampling times of 2 ms or greater.

In other environments metallic and paramagnetic components are present, and there is a pressure to make measurements at 500  $\mu\text{s}$  or less. In these cases measurement will be probing the brittle-plastic phase transition, not the brittle-liquid phase transition, leading to spuriously low pore-size measurements.

Thus an investigation has been commenced to further investigate the suitability of a-polar liquids to NMR-C measurements (which has a long history), but this time focusing on the dynamics of the systems in pores, with a view to making successful NMR-C measurements at short times.

### **Dynamics: NMR Relaxation study**

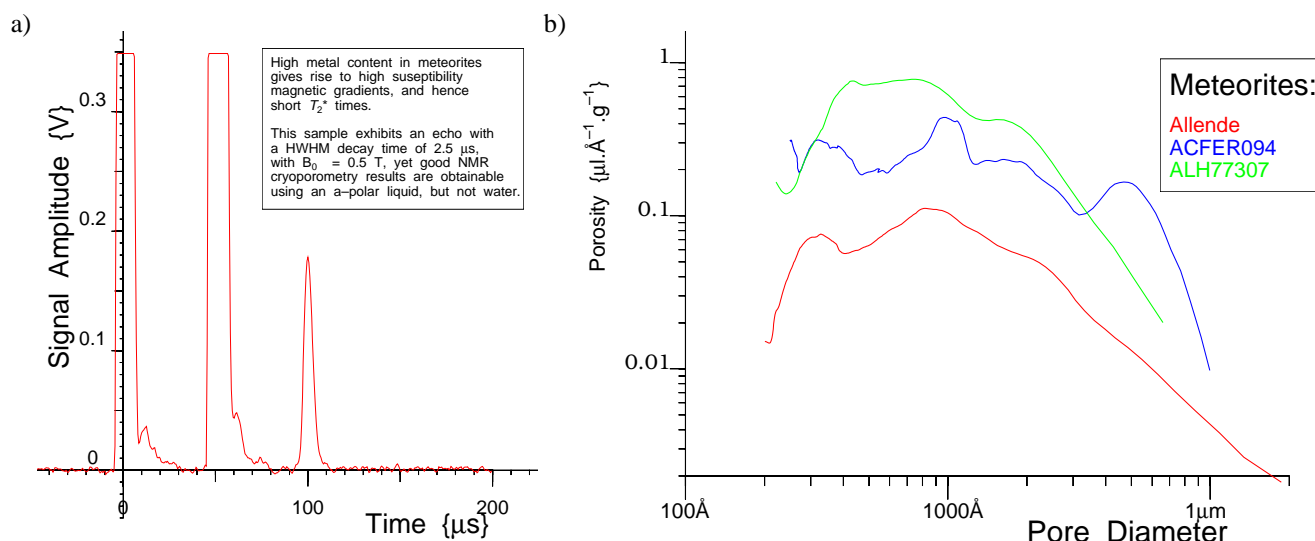
Cyclohexane has a long and successful history as a probe liquid for NMR-C, but it has a bulk-phase plastic state between the brittle and liquid phases; thus it is well known that measurements that employ it need to be performed with a  $2\tau$  echo time of around 20 ms. Benzene has also been used, and it was suspected that the similarity of geometric shape to cyclohexane might lead to a rotator state in the pores.

Measurement with Benzene in SBA-15 show that below about -30 C the pore liquid freezes to what may be a plastic phase, with a  $T_2$  in the region of 700  $\mu\text{s}$ , that slowly decreases and becomes Gaussian-like as the temperature is lowered further.

For the alkane Dodecane in SBA-15, below about -30 C the pore liquid freezes to what may be either a brittle or plastic phase, however the  $T_2$  is in the region of 160  $\mu\text{s}$ , which is appropriate for fairly short  $\tau$  NMR-C studies.

For the alkane Tetradecane in SBA-15, below about -10 C the pore liquid freezes to what may be either a brittle or plastic phase, however the  $T_2$  is in the region of 80  $\mu\text{s}$ , which is appropriate for even shorter  $\tau$  NMR-C studies.

The exponential behaviour of the FIDs just below the pore melting temperature may indicate that the Dodecane and Tetradecane are in a predominantly rotator state, as the translational motion will be greatly reduced.



**FIGURE 3.** a) NMR spin-echo trace for an a-polar liquid in meteorite ALH77307, showing extreme shortening of  $T_2^*$  due to high magnetic gradients from metallic content, with associated reduction in  $T_2$ . b) NMR cryoporometry pore-size distributions, measured at short  $2\tau$  times, using an a-polar liquid without a significant plastic crystal component, for three meteorite samples: Allende, Acfer 094 and ALH77307.

## APPLICATIONS: METEORIC PORES; CONCLUSIONS

An application of this study relates to measuring pore-size distributions in short relaxation time materials such as high-iron clays, rocks and cement. An extreme examples of such materials is provided by meteorites [8].

Figure 3a shows a spin-echo sequence for an a-polar liquid in a meteoritic sample, in a 0.5T field, with extreme broadening due to metallic component induced gradients. Figure 3b shows that using an a-polar liquid in meteoric samples preliminary pore-size distributions can be successfully measured, using NMR cryoporometry.

A significant conclusion from the neutron diffraction cryoporometric studies is that plastic ice forms at ice-vapour interfaces. It is well known from the study of the bulk mechanics of sea ice, snow-packs and glaciers, that modeling must be done with a viscous-plastic (VP) or elastic-viscous-plastic (EVP) model [9]; this deduction that the ice may be in a state of enhanced rotational motion at each of the myriad of ice-vapour interfaces in compressed snow-packs, leading to a continual breaking and forming of the hydrogen bonds, may be relevant.

The successful application of NMR cryoporometry to the study of meteoric samples is an important application for this non-destructive technique, and opens the way to study 'difficult' geological and constructional samples.

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