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PHASE RELATIONS FOR WATER AND ICE IN CONFINED GEOMETRY

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Abstract.

A brief survey is given of the structural characteristics of water at low temperatures in the normal and super-cooled states using neutron diffraction. Similar studies are presented for D_2O water in mesoporous sol-gel silicas showing the depression of the nucleation temperature, the effects of fractional filling and the formation of cubic ice I_c in the pores. Preliminary data is also presented for both neutron and x-ray diffraction studies of water in the ordered MCM41 silica, showing the deep super-cooling and the reversible phase transformation between water and cubic ice. The importance of hydrogen-bonded networks and the development of long-range correlations are used to provide an explanation of the observations. Further work is in progress.

1. Introduction

The phase diagram for ice consists of a large number of crystalline phases dependent on various geometries of hydrogen-bonded networks. The importance of the hydrogen-bond remains in the disordered phases of liquid water and amorphous ices. The effects are clearly displayed in the super-cooled regime where there are significant structural changes as a function of temperature. The liquid density is reduced towards that of ice I and there is a steady evolution of the hydrogen-bonded connectivity towards the continuous random network of tetrahedral bonds that characterises the structure of low-density amorphous ice.

If the water is confined within the geometry of a mesoporous solid (usually silica), the nucleation temperature is depressed by an amount that is inversely proportional to the pore size. Furthermore, the ice formed under these conditions is not normally of the form ice I_h produced from the bulk phase. The phase relationships for ice in confined geometry are therefore of interest and have been investigated by neutron and x-ray diffraction studies. The following sections describe some of the recent results.

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2. Diffraction formalism

For neutron diffraction by heavy water, D_2O, the measured molecular structure factor $S_M(Q)$ may be written as

$$S_M(Q) \quad = \quad f_1(Q) \quad + \quad D_M(Q)$$

where $f_1(Q)$ is the form-factor and $D_M(Q)$ represents inter-molecular terms that define the liquid structure. The composite pair correlation function, $\bar{g}(r)$, may be evaluated from the Fourier-Bessel transform

$$d(r) \quad = \quad 4\pi\, r\, \rho_M[\overline{g}(r) - 1] \quad = \quad \frac{2}{\pi}\int_0^\infty \, Q\; D_M(Q)\; \sin Qr\; dQ$$

where ρ_M is the molecular density. For D_2O, the partial functions are weighted according to

$$\bar{g}(r) \;\; = \;\; 0.092\, g_{OO}(r) \;\; + \;\; 0.422\, g_{OD}(r) \;\; + \;\; 0.486\, g_{DD}(r).$$

For temperature variation studies it is convenient to use a difference function analysis procedure where

$$\Delta S_M(Q,T,T_0) \quad = \quad S_M(Q,T) \ - \ S_M(Q,T_0) \quad = \quad \Delta D_M(Q;T,T_0)$$

for a temperature T relative to a reference temperature T_0. The corresponding spatial function, $\Delta d_L(r;T,T_0)$, may be evaluated from the transform of $\Delta D_M(Q;T,T_0)$. Equivalent expressions may be written for the x-ray case where the scattering is predominantly from the oxygen atoms and the b-values are replaced by the appropriate atomic form-factors, which are Q-dependent.

3. Structural Characterisation of Low-temperature Water and Amorphous Ice

Neutron diffraction studies have been made of ‘bulk’ super-cooled water down to temperatures 35^o below the normal nucleation temperature. The density decreases by 8% and the structure changes significantly with temperature due to the development of long-range correlations [1] as shown in Fig 1. Low-density amorphous ice is made by vapour-deposition onto a cold substrate plate. The neutron diffraction pattern has a pronounced peak at 1.7 $\text{Å}^{-1}$and the $d(r)$ function has well-developed features extending to 20 Å and beyond. The structure corresponds to that of a fourfold coordinated random network based on approximately linear hydrogen-bonds. All of the specific features in the $d(r)$ curve (Fig.1) can be explained by correlations within the network. In this context it can be seen that the structural changes in super-cooled water can be viewed as an increasing build-up of hydrogen-bond connectivity as the temperature is reduced. In effect the structure of the deeply-supercooled liquid is evolving towards that of amorphous ice but this metastable state is interrupted by the process of nucleation and crystallite growth. It is also clear that the amorphous ice phase undergoes a phase transition to cubic ice at 140K so although the structural characteristics seem closely related there is a temperature regime where neither phase can exist on an experimental timescale.

4. Experimental results for water/ice in mesoporous silicas

4.1. SOL-GEL SILICAS

Neutron diffraction results for D_2O in sol-gel silicas have been presented previously [2] and also covered in a recent review [3]. The main effect is a shift in the position of the main diffraction peak $Q_0(T)$as a function of temperature. This feature indicates an enhanced hydrogen-bonding for the confined water compared with that of the bulk liquid and corresponds

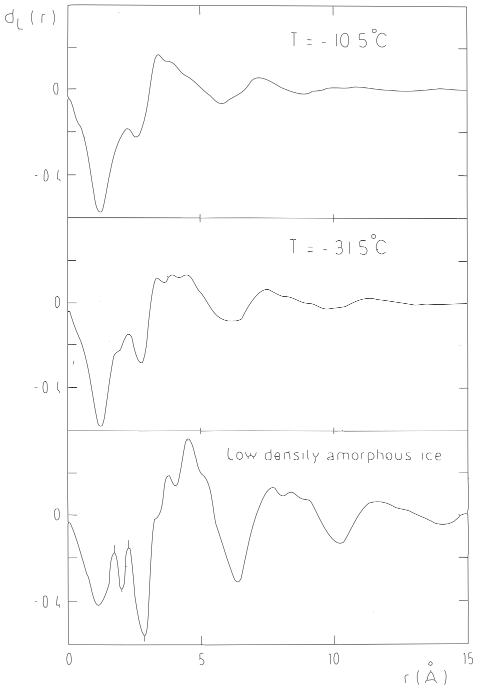


Figure 1. Spatial correlations in deeply-supercooled water and low-density amorphous ice from neutron diffraction measurements[1].

to a shift of approximately 15°C for 90 Å pores, as shown in Fig 2. The nucleation temperature is also depressed and depends on the pore size.

4.2. PARTIALLY-FILLED PORES

It has been suggested that water in the interfacial region close to the hydrophilic interface has different properties due to the bonding to surface siloxyl groups. The effective range of this influence has remained a controversial topic for many years but the current consensus is that it is restricted to a few molecular layers. Comparative studies [3, 4] using the temperature difference approach for fractional fillings of 0.4, 0.6 and 1.0 were unable to detect any significant variations and showed that the separate $\Delta D_M(Q;T,T_0)$ and $\Delta d_L(r;T,T_0)$ curves scaled almost exactly according to the filling factor. This surprising result suggests that there is minimal perturbation to the water structure in the interface region. The significance of this observation will be discussed in Sec 5.

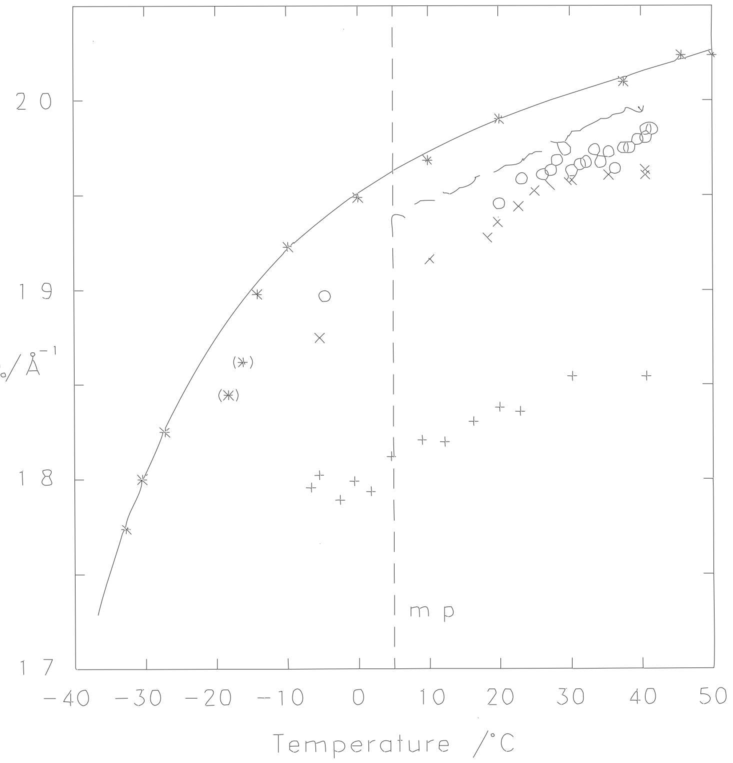


Figure 2. Variation in the position of the main diffraction peak $Q_0(T)$ as a function of temperature for bulk and confined water.

4.3. ICE NUCLEATION IN SOL-GEL SILICAS

Neutron diffraction results [4, 5] have shown that the super-cooled water nucleates with the formation of cubic ice I_c rather than hexagonal ice I_h formed from the bulk state. This unexpected behaviour appears to be related to the nucleation and growth mechanism in the pores as ice I_h is formed in large pores. The effect can be most conveniently demonstrated for the partial filling of differently-sized pores and the use of a high-resolution diffractometer. Fig.3 shows the diffraction pattern in the region of 1.7 Å^{-1} from several samples where the effective thickness of the water layer is approximately 20 Å. The characteristic signal for ice I_h consists of a triplet whereas that of ice I_c comprises a single central peak. The results show that a thin water layer in a large pore nucleates to form pure hexagonal ice but in a more restricted volume there is an asymmetric peak profile suggesting a defective form of cubic ice. There is a possibility that this profile can be explained on the basis of stacking faults in the ‘abcabc’ layers but the situation is complicated and there is no convincing explanation of the observed results. Further discussion is deferred to Sec 5.

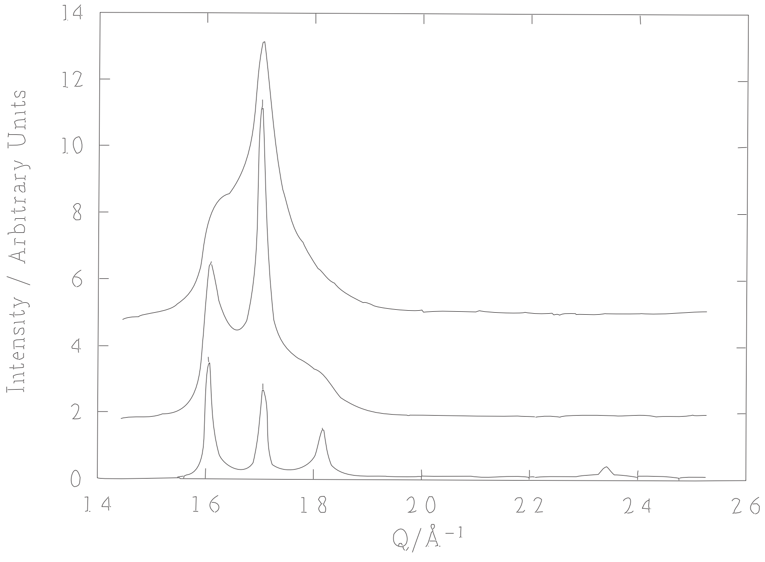


Figure 3. The main diffraction peak after nucleation of ice in different pore-size silicas.

4.4. WATER/ICE IN MESOPOROUS SILICAS; NEUTRON DIFFRACTION

The MCM-type silicas [6] provide an important class of ordered mesoporous solids where the geometry is well defined. They are produced via the sol-gel process using a liquid crystal template and are calcined to give an ordered array of channels with diameters in the 25-35 Å range. There are two forms shown in Fig.4 based on the hexagonal array of parallel pores (MCM41) or an inter-twined array of branched pores based on the cubic phase (MCM48).

Neutron diffraction data [3, 6] have been taken for both systems and results are shown in Fig.5a for D_2O in MCM41at several temperatures after subtraction of the substrate scattering contribution. The liquid undergoes deep supercooling and nucleates to cubic ice at approximately 45^oC below the normal freezing point of the bulk sample. Furthermore, the transformation between the liquid and crystal phases is completely reversible without any hysteresis. Consequently, there appears to be a first-order phase transition between two states that would both be in a metastable condition for the bulk state at this temperature. The use of a difference function procedure gives the $\Delta d_L(r; T, T_0)$ function shown in Fig.5b, where the build-up of long-range spatial correlations can be seen to be similar to the features of Fig 2. It is clear that there is a continual enhancement of the hydrogen-bonding network as the temperature is reduced.

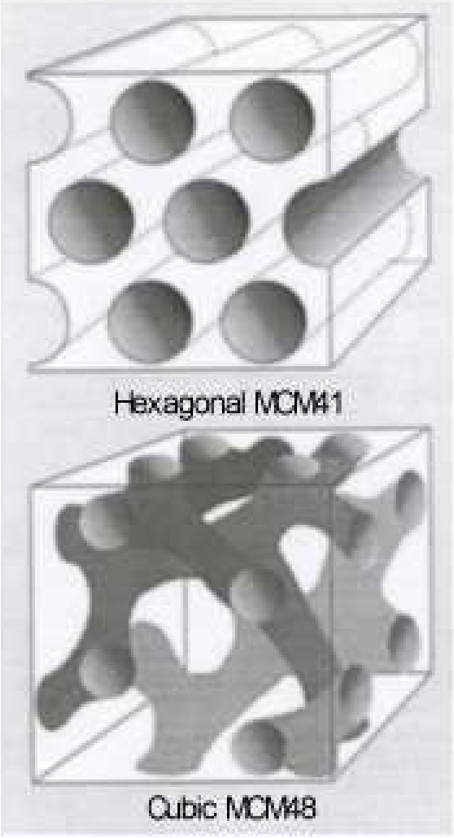
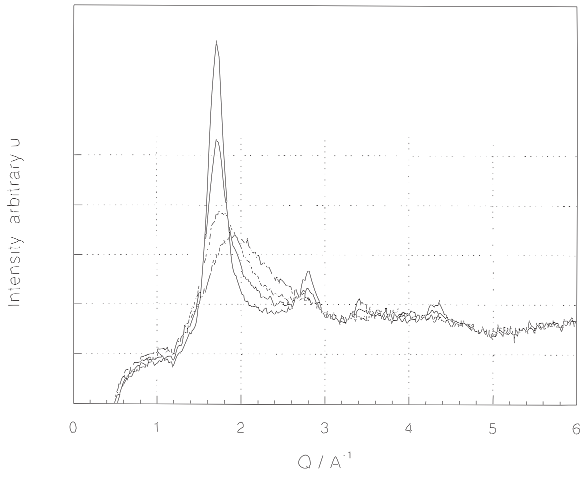


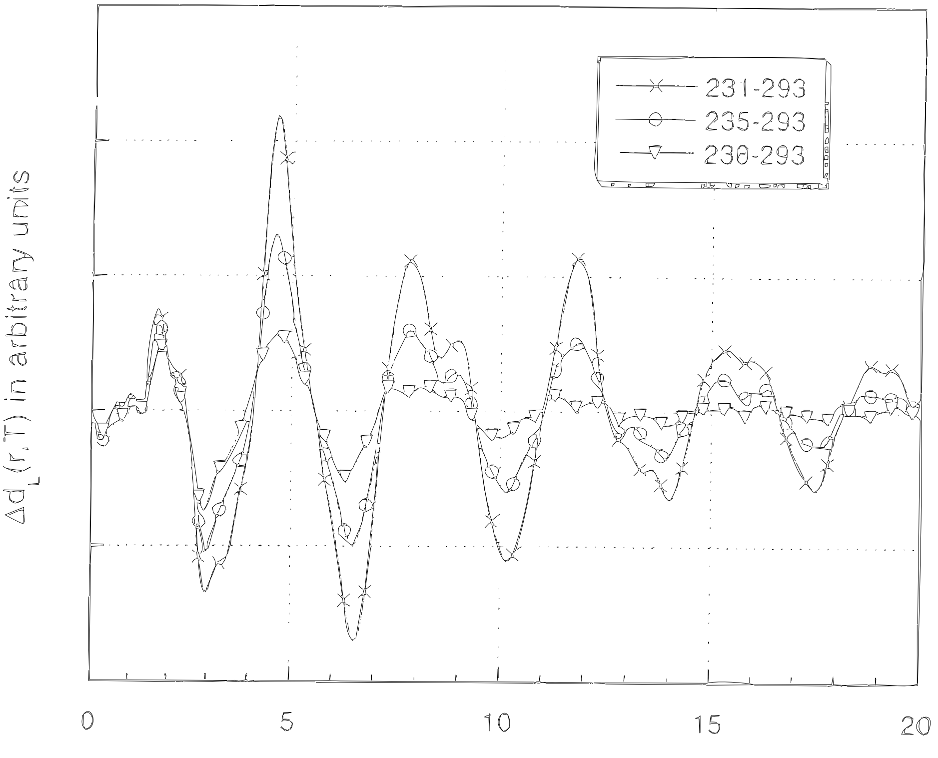
Figure 4. The mesoporous structure of MCM41 and MCM48 silicas.

4.5. WATER/ICE IN MESOPOROUS SILICAS; X-RAY DIFFRACTION

In order to study other aspects of the deeply-supercooled state and nucleation characteristics, an x-ray diffraction study [7] using synchrotron radiation was undertaken .A sample of the preliminary results is given in Fig.6 based on a difference function analysis. It was found that ice nucleation occurred at a higher temperature than expected but it is unclear whether this occurrence is due to the perturbation of the sample by the x-ray beam or due to excess water on the outside of the pores. The figure shows that hexagonal ice is initially formed but also that the central peak



a) diffraction results.



b) the change in the spatial function $\Delta d_L(r;T,T_0)$.

Figure 5. Neutron diffraction data for supercooled water in MCM41 silica.

of the triplet increases in intensity at the lower temperatures corresponding to the formation of cubic ice. A puzzling feature of the measurements was an apparent change in the relative intensities of the triplet peak even when the temperature was stable. This behaviour suggests that there are dynamic changes in the ice structure on a timescale of minutes. The beam-size was 2 x 3 mm so many crystallites contribute to the diffraction pattern and it seems unlikely that this observation can be the result of any preferred orientation in the sample. The natural conclusion is that the ice structure is itself changing and that the average over the fluctuating Bragg intensity is being observed in the datasets. Clearly, a more detailed investigation will be needed to isolate the separate time and temperature dependence but the obvious conclusion is that the nucleating ice is not in a stable equilibrium state.

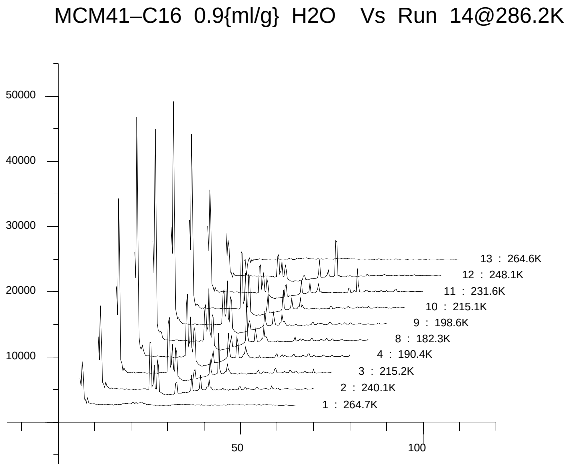


Figure 6. Temperature difference functions for x-ray scattering by water in MCM41 silica.

The changes with temperature can also be seen in the small-angle scattering region. At low Q-values, the SAXS intensity profile results from the ordered array of the cylindrical pores and has a similar shape to that for the liquid crystal used as the template. The intensity for this region shows a systematic variation with temperature and is highest below 200K, the lowest temperatures of measurement. Furthermore the intensity falls as the sample is warmed to its original temperature.

The origin of the SAXS signal is from the contrast between the ρ-value of silica and ice; typical relative values are 9.3 for ice I_h and approximately 24 for the silica substrate. The large change in intensity is therefore difficult to understand as the ρ-values are not expected to change much with temperature. The only other possibility is that there are inhomogeneities within the ice itself leading to a variation in density across the pore volume that is then convoluted with the liquid crystal form-factor. If so, this phenomenon would imply a partial fragmentation of the ice at low temperatures and a healing or annealing effect on warming. It is, of course, possible that the ice is under pressure from the changes in density within the restricted volume but it is still difficult to provide a self-consistent picture that fully explains the observations. Further measurements under carefully controlled conditions and checks for reproducibility will be required to understand these complex new results. It is hoped to make these measurements in the near future [8]

Conclusions and Future Work

The picture that emerges from these investigations is that the deeply-supercooled liquid state depends on the systematic evolution of the hydrogen-bonded network with reducing temperature. The properties vary in a predictable manner despite the density maximum and the unusual behaviour of the super-cooled state. In a similar manner, the properties of low-density amorphous ice can be understood in terms of a continuos random network of hydrogen-bonds. Although quantitative agreement with the experimental results has not been obtained from simulation studies, it is well recognised that the space-filling characteristics of the tetrahedral bonding play a central role in the behaviour. What remains as a challenge to present understanding centres on the phase relations between the ordered and disordered states, whether in the crystalline solid, amorphous solid or liquid. The present work addresses the relationship between water and amorphous ice with crystalline ice I, using confined geometry to provide deep supercooling of the liquid.

Under bulk conditions, hexagonal ice I_h forms naturally as water is cooled. However, it appears that the initial phases of nucleation and growth involve the formation of a defective seed crystallite of ice I_c. The reasons for this behaviour are unclear and are probably linked to the stability of small H-bonded clusters in the liquid. As the temperature is further reduced, the network connectivity is increased and the longer-range correlations become more important. The effects of the confined geometry give an effective temperature shift so that the network becomes more developed, molecular motion is more restricted and the nucleation process is inhibited. The effect of pressure within the capillaries cannot be ignored but it cannot be simply evaluated. The most important parameter is the density of the confined water in the pores and its variation with temperature but experimental methods to determine this value are problematic; one possibility is currently under investigation [9].

The effect of the pore size (Fig 3) suggests that ice I_h is the preferred crystalline phase for large extensions of connected water, whether as a volume (3D) or a thin layer (2D). It seems likely that this principle will remain for hydrophobic as well as hydrophilic interfaces but there is, as yet, no experimental verification since most of the studies are naturally based on the wide range of silicas that are available. Some additional studies on partially-hydrophobic samples are needed but are difficult and have not been attempted in any systematic manner. The obvious extension to systems of biological significance is a natural development and also the associated prevention of crystallization in cryo-protection processes.

Another puzzling aspect of the current studies is the apparent changes that occur in the diffraction [and SAS] pattern below the onset of ice nucleation. This phenomenon suggests that there is a much more complex behaviour of the confined ice than might have been expected. The fact that the water/ice system continues to give unexpected results is, itself, possibly no surprise – it seems that the more we learn about this fascinating system, the less we understand about the nature of collective hydrogen-bonded systems. The next decade should see further advances in the linking together of experimental, simulation and theoretical developments to provide a clearer picture but it seems inevitable that water and ice will continue to baffle us for a little while longer. The mysteries of water will remain as a major scientific challenge for the foreseeable future.

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References

1. M-C. Bellissent-Funel et al, Europhys. Lett. **2, 241 (1984)**
2. **D.C.Steytler, J.C.Dore and C.J.Wright, Mol. Phys. 56,1001 (1985) and papers cited therein**
3. **Structural studies of water in confined geometry, J.Dore, Chem. Phys.258, 327 (2000).**
4. **J.M.Baker, PhD thesis, University of Kent, (1996)**

5. J.M.Baker, J.C.Dore and P.Behrens, J. Phys. Chem. B1001, 6226 (1997)
6. P.Behrens and G.Stucky Angwe. Chem. Int Ed Engl. 32, 696 (1993)
7. J.C.Dore, J.B.W.Webber, M.Hartl and A. Mazuelas, unpublished data; report in ESRF Annual Review 2001
8. Neutron and x-ray experiments for water in MCM silicas are already planned.
9. The use of variable isotopic substitution for H_2O/D_2O mixtures can be used in SANS studies to give the temperature dependence of the density but the determination of absolute values poses significant problems.