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Structural study of water confined in porous glass by neutron scattering

M.-C. Bellissent-Funel and J. Lal

Laboratoire Léon Brillouin (CEA-CNRS), CE-Saclay, 91191 Gif-sur-Yvette Cedex, France

L. Bosio

Laboratoire Physique des Liquides et Electrochimie (CNRS), 10, rue Vauquelin, 75231 Paris Cedex 05, France

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In order to study the structural properties of water at interfaces, we performed neutron scattering experiments of water confined inside interconnected pores of Vycor glass. The structure factors and the corresponding radial distribution functions of the confined water have been determined as a function of temperature from 35 °C down to -100 °C and for two levels of hydration of the glass (full and partial hydration). At 27 °C, the structure factor of confined water is very similar to that of bulk water. When decreasing the temperature, we show that it is possible to supercool water inside pores of Vycor but not to the extent expected for such a small confining space. In fact the presence of large hydrophilic silica interface enhances the nucleation of ice. The observed phase of ice is the cubic ice which appears at about -18 °C in the full hydrated Vycor. The other interesting observation is a greater degree of supercooling of water in partially hydrated samples of Vycor compared to fully hydrated ones. Moreover, the presence of a small amount of liquid water down to -40 °C is identified.

I. INTRODUCTION

The problem of structure of liquids in restricted geometries and especially at interfaces concerns a great variety of physical situations occurring in surfaces, lamellar systems, amorphous systems, ionic polymers, and biomolecular systems. Neutron diffraction measurements have been made on water and cyclohexane in various types of porous silicas.¹⁻⁵ Also recent small angle neutron scattering studies of adsorbed water in porous Vycor glass have shown a diffuse supercooling transition.⁶ The structure of water in clay minerals has been studied by Hawkins and Egelstaff⁷ and Soper.⁸ Wiggins⁹ who has studied the structure of water in polymer membranes contends that the properties of water are profoundly changed in the hydrophobic pockets of nanometer dimensions. The structure of water confined in a hydrogel has been recently studied by x-ray and the distortion seen at the level of the second molecular neighbors has been attributed to the bending of the H-bonds.¹⁰ Our main interest deals with the structural behavior of water at interfaces and in the comparison with that of bulk water. In order to examine the effect due to interfaces and thus the role of the confinement, we studied water confined in the narrow, randomly distributed and three dimensionally interconnected pores of the silica glass "Vycor."

We report here on the results of the structure of water confined in Vycor for two levels of hydration (full and partial hydration) and in a range of temperature from 35 °C down to -100 °C. The experiments have been performed by neutron scattering on the 7C2 spectrometer of the Reactor Orphée of the Laboratoire Léon Brillouin, at Saclay.

II. THEORY

The basic theory for studies of neutron scattering from molecular systems is well known and only the essentials will be repeated here.¹¹

The liquid structure factor $S_M(Q)$ can be written in terms of a molecular form factor $f_1(Q)$ and a difference function $D_M(Q)$ which contains all the intermolecular contributions, i.e.,

$$S_M(Q) = f_1(Q) + D_M(Q), \quad (1)$$

where Q is the scattering wave vector.

For D_2O molecules, $f_1(Q)$ is given by

$$f_1(Q) = [b_O^2 + 2b_D^2 + 4b_O b_D j_0(Qr_{OD}) \exp(-\gamma_{OD} Q^2) + 2b_D^2 j_0(Qr_{DD}) \exp(-\gamma_{DD} Q^2)] / (b_O + 2b_D)^2, \quad (2)$$

where r_{OD} is the intramolecular oxygen-deuterium distance and $r_{DD} = 2r_{OD} \sin(1/2 \beta)$ for an intramolecular bond angle β , $j_0(x) = (\sin x/x)$ and $\gamma_{ij} = 1/2 \langle u_{ij}^2 \rangle$, where $\langle u_{ij}^2 \rangle$ is the mean-square amplitude of the displacement from the equilibrium position due to the normal mode vibration of the molecule. b_O and b_D are the coherent scattering lengths of oxygen and deuterium atoms ($b_O = 0.5805 \times 10^{-12}$ cm, $b_D = 0.6674 \times 10^{-12}$ cm).

The total pair-correlation function $g(r)$ is related to the Fourier transform of $S_M(Q)$ by

$$d(r) = 4\pi r \rho_M [g(r) - 1] = \frac{2}{\pi} \int_0^\infty Q [S_M(Q) - S_M(\infty)] \sin Qr dQ, \quad (3)$$

where $S_M(\infty) = (b_O^2 + 2b_D^2)/(b_O + 2b_D)^2$ is the asymptotic value of $f_1(Q)$ at large Q and ρ_M is the molecular number density.

The function $d(r)$ is a combination of the separate partial correlation functions and includes sharp peaks due to the intramolecular distances. It is more convenient to remove the intramolecular terms by subtracting the molecular form factor from $S_M(Q)$ to give $D_M(Q)$, which may be transformed by

$$d_L(r) = 4\pi r \rho_M [g_L(r) - 1] = \frac{2}{\pi} \int_0^\infty Q D_M(Q) \sin Qr dQ \quad (4)$$

to give the pair-correlation functions $d_L(r)$ and $g_L(r)$ for the intermolecular terms only. The composite function $g_L(r)$ [or $d_L(r)$] consists of a weighted sum of partial terms which for neutron diffraction by D_2O is expressed by

$$g_L(r) = 0.489g_{DD}(r) + 0.421g_{OD}(r) + 0.090g_{OO}(r), \quad (5)$$

where the dominant contributions concern the D–D and O–D spatial correlations.

For measurements at different temperatures, it is interesting to introduce the difference function method^{12,13} and thus, to define the function $\Delta D_M(Q, \Delta T)$ as

$$\Delta D_M(Q, \Delta T) = S_M(Q, T_1) - S_M(Q, T_2) \quad (6)$$

with $\Delta T = T_1 - T_2$. This works provided that $f_1(Q)$, i.e., the molecular conformation remains unchanged with temperature.

In case of heavy water which has a density maximum at 11 °C a refinement of the difference function method eliminates the correction term due to density variation by defining the isochoric temperature derivatives (ITD) (Ref. 14) for a pair of temperatures T_1 and T_2 such that the density of water is the same. The Fourier transform $\Delta d_L(r, \Delta T)$ would help to investigate the effects of hydrogen bonding on the intermolecular distribution function and get complementary information about the structure of confined water as compared to that of bulk water.

III. EXPERIMENTAL DETAILS AND DATA ANALYSIS

A. Sample preparation

The samples were elaborated from Vycor brand porous glass No. 7930 which is a product of Corning Glass Works.¹⁵ Vycor glass is prepared by heating a homogeneous mixture of boron oxide glass and silica glass and then quenching this mixture to a temperature below the coexistence and spinodal curve where it phase separates into two mutually interpenetrating regions. At a certain stage of separation the boron rich region is leached out leaving behind a silica skeleton with a given distribution of pore sizes. For the samples of cylindrical geometry used in this experiment the average pore size is 50 Å as claimed by the manufacturer.¹⁵

We adopted the following procedure for the preparation of the Vycor samples used for the differential thermal analysis and for the neutron scattering experiments. In the

TABLE I. Characteristics of the Vycor samples.

Samples	Regain
Full hydration	24.5%
Partial hydration	13.6%

latter case, the Vycor samples were cylinders of diameter 7.2 mm and height 76 mm while in the former one, they were very small pieces. The Vycor samples were immersed in 30% hydrogen peroxide and heated up to 90 °C for a few hours to remove any organic impurities absorbed by the glass. They were washed in distilled water in order to remove the hydrogen peroxide and stored in heavy water for deuteration. Then the deuterated Vycor samples were heated at 90 °C and vacuum dried until they are translucent and clear, defining what we called “dry Vycor sample.”

The fully hydrated sample was obtained by immersing a dry Vycor sample in D_2O for half an hour in a glove box filled with helium.

At full hydration Vycor glass absorbs heavy water up to 25% of its dry weight. The partially hydrated sample was obtained by drying a fully hydrated one until the desired level of hydration is reached. Water content was determined by

$$\left(\frac{\text{wt. of water} \times 100}{\text{wt. of dry Vycor}} \right) \% = \% \text{ regain.} \quad (7)$$

The characteristics of the samples used in this study are summarized in Table I.

Before starting the neutron scattering experiments the samples have been characterized by differential thermal analyses.

B. Differential thermal analysis

A differential thermal analysis method was used to observe the freezing of liquid water and the melting of ice in porous silica. We noted that the water–ice phase transformation behavior varies with water content. For partially hydrated Vycor, the crystallization occurs in the temperature range from -21 to -26 °C, depending on the sample [Fig. 1(a)] and we can see that the freezing of liquid water starts abruptly which indicates that the pores are interconnected. The melting of ice occurs at a temperature lower than the bulk normal melting point (4 °C for D_2O) and starts around -7 °C. Such a melting point depression agrees with the quoted pore volume and the law found by Kennie and Clifford.¹⁶

For fully hydrated Vycor, two exothermic peaks are observed on cooling [cf. Fig. 1(b)]. The first one, between -10 and -18 °C, can be attributed to extra pore water; the second peak arises in the same range of temperature as the one observed in the partially hydrated Vycor, either as a broad peak [as seen in Fig. 1(b)] or sometimes as a sharp one. In the melting process, two endothermic peaks appear; this two phase melting agrees well with a previous observation.¹⁶

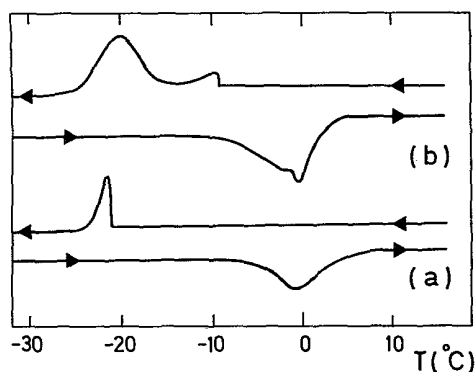


FIG. 1. Results of differential thermal analysis (at scan speed of 2°/min) related to (a) partially hydrated Vycor and (b) fully hydrated Vycor.

It has to be noticed that there is less nucleation of ice in emulsified supercooled water at -31.5°C (Ref. 13) than in water inside pores. The reason might be the strong surface interaction of the first layer of water molecules with the large hydrophilic surface of silica in Vycor, due to interconnected pores.

We shall see further that the nucleation sites induce the formation of I_c cubic ice which reverts to hexagonal ice I_h just before the melting.

C. Neutron scattering experiments

The experiments were done at the reactor Orphée at Saclay, on the 7C2 spectrometer which is equipped with a BF_3 position sensitive detector with 640 cells; the angular step between two adjacent cells is 0.2° which leads to a maximum diffraction angle 2θ of 128° . The wavelengths used in the experiment were 0.698 and 0.581 \AA allowing it to cover a range of scattering wave vectors ($Q=4\pi \sin \theta/\lambda$) extending from 0.35 to 19 \AA^{-1} . The samples were held in containers of thin-walled vanadium (0.1 mm thick) with internal diameter equal to 8 mm inside a helium cryostat. The samples used in this study were fully hydrated Vycor, partially hydrated Vycor (cf. Table I) and dry Vycor. The temperature covered in the experiment was 35 to -100°C . The data were corrected for background and absorption effects, using the classical Paalman and Pings procedure¹⁷ with the calculated values of the total (absorption + scattering) linear coefficients $\mu_T^V=0.381 \text{ cm}^{-1}$, $\mu_T^{V+W}=0.583 \text{ cm}^{-1}$ (fully hydrated sample), $\mu_T^{V+W}=0.513 \text{ cm}^{-1}$ (partially hydrated sample), at $\lambda=0.698 \text{ \AA}$ and at room temperature.

Figures 2(a) and 2(b) show the spectra related to the fully hydrated Vycor and dry Vycor at 27°C . The intensity $I(Q)_{V+W}$ scattered by a sample may be written as¹

$$I(Q)_{V+W}=I(Q)_V+I(Q)_W+I(Q)_{VW} \quad (8)$$

in terms of contributions from silica phase $I(Q)_V$ (Vycor being predominantly consisting of silica), from water phase $I(Q)_W$ and also from an additional term $I(Q)_{VW}$ due to correlation between the silica and water phases.

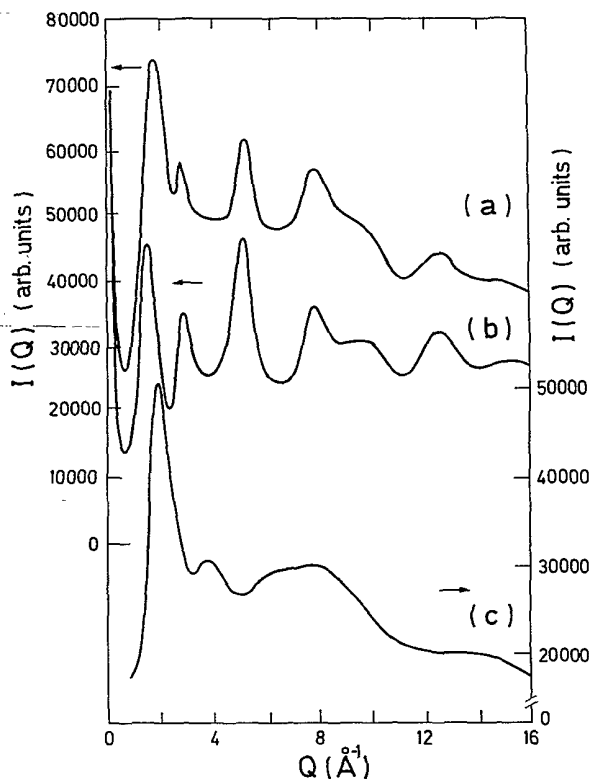


FIG. 2. (a) Spectrum of Vycor fully hydrated with D_2O at 27°C . (b) Spectrum of dry Vycor at 27°C . (c) Spectrum of confined D_2O at 27°C resulting from Eq. (9).

Concerning this additional term $I(Q)_{VW}$ it has to be noticed that the silica surface is strongly hydrophilic. The extent of the interaction is roughly over two molecular layers, i.e., a distance of $3.1\text{--}7 \text{ \AA}$.¹⁶ However, the surface hydroxylic groups are already present in the dry Vycor. In such a case, the ratio $I(Q)_{VW}/I(Q)_W$ is assumed to be small and we do the following subtraction:

$$I(Q)_W=I(Q)_{V+W}-\alpha I(Q)_V^d, \quad (9)$$

where $I(Q)_V^d$ is the intensity scattered by the dry Vycor.

The coefficient α depends on the composition of the samples, and particularly on the proportion of Vycor in them. For the full hydrated sample $\alpha=0.75\pm 0.01$ and for the partial one $\alpha=0.80\pm 0.01$. The spectrum $I(Q)_W$ depicted in Fig. 2(c) contains both $S_M(Q)$ and the incoherent contribution together with the multiple and inelasticity effects. We used an empirical method, which was shown to be reliable for making corrections for the recoil and inelasticity effects in the case of neutron scattering by water.¹⁸

IV. RESULTS AND DISCUSSION

A. Structure factors $S_M(Q)$ and pair correlation functions $d_L(r)$

Figures 3(a) and 3(b) show plots of $S_M(Q)$ of confined water at 27 and 35°C from fully and partially hy-

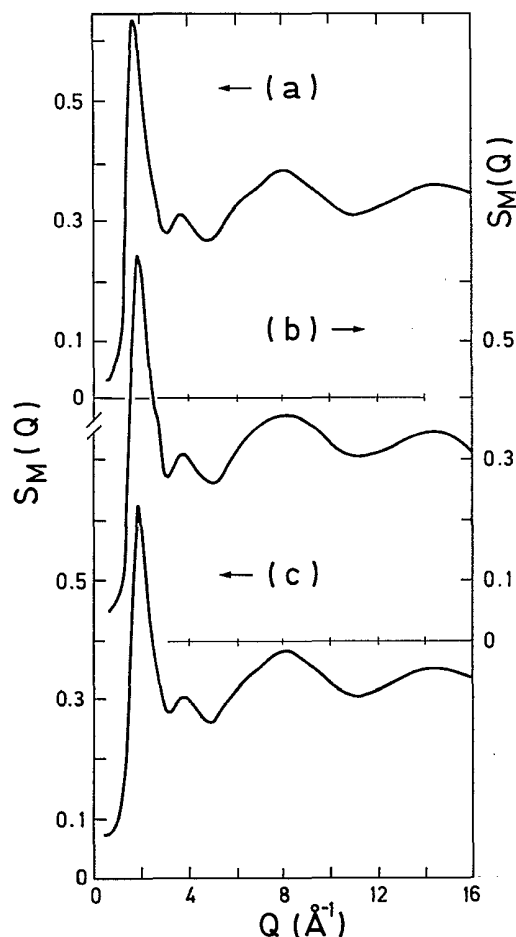


FIG. 3. $S_M(Q)$ for (a) confined D_2O from fully hydrated Vycor (27 °C); (b) confined D_2O from partially hydrated Vycor (35 °C) compared with (c) bulk water (27 °C) (Ref. 18).

drated Vycor, respectively, compared with that of bulk D_2O at 27 °C [Fig. 3(c)].

It appears that the structure factor of confined water from fully hydrated Vycor is very similar to that of bulk water¹⁸ at the same temperature. We obtain a comparable agreement for the partially hydrated Vycor. This result justifies the assumption made in the data treatment [Eq. (9)] where we supposed that the $I_{VW}(Q)$ contribution was negligible. In Fig. 4 we give the corresponding pair correlation functions of confined water from fully and partially hydrated Vycor as compared with that of bulk water.

When the temperature is lowered a striking feature of $S_M(Q)$ is the displacement of the main diffraction peak position towards smaller Q values with decreasing temperature as observed for bulk water¹⁹; a sharpening of this main diffraction peak is also observed. Another interesting feature is that we observe like in the differential thermal analysis measurements, supercooling of water to a much lower temperature of -27 °C in a partially hydrated sample compared to a fully hydrated sample (-18 °C). It seems that the confinement of the water favors the nucleation of cubic ice which appears superimposed on the spec-

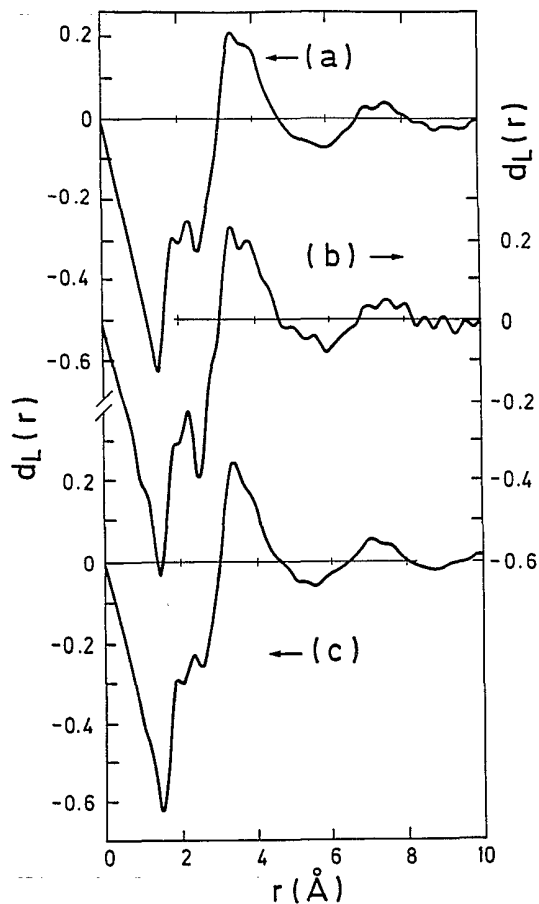


FIG. 4. $d_L(r)$ for (a) confined D_2O from fully hydrated Vycor (27 °C); (b) confined D_2O from partially hydrated Vycor (35 °C) compared with (c) bulk water (27 °C) (Ref. 18).

trum of liquid water and whose proportion can be deduced from the intensity of the (111) Bragg peak. The proportion of cubic ice increases with decreasing temperature. In fact, at -100 °C, the spectrum of confined water looks similar to that of cubic ice²⁰ (Fig. 5) as opposed to hexagonal ice observed in bulk samples. The appearance of ice I_c is surprising as this metastable phase of ice has only been formed at much lower temperature (< -120 °C) and is never obtained on cooling liquid bulk water. For example it appears when heating up low density amorphous ice.²¹ This observation of cubic ice has already been reported in spherisorb silica.³ The interplay between the geometry of the confining walls and the structure of underlying silica surfaces in Vycor might both influence the formation of Bragg-type peaks of cubic ice and hinder formation of hexagonal crystallites. The structure of hexagonal and cubic ice are very similar, they differ only in the placement of the oxygen atoms. The oxygen are arranged in hexagonal rings; the conformation being boat form in case of hexagonal ice and chair form in cubic ice. The more stable hexagonal structure has $ABA...$ layered sequence, whereas cubic ice is in $ABCA...$ sequence.²² In case of hexagonal ice, two planes of consequent hexagonal (oxygen) lattice superimpose, we find

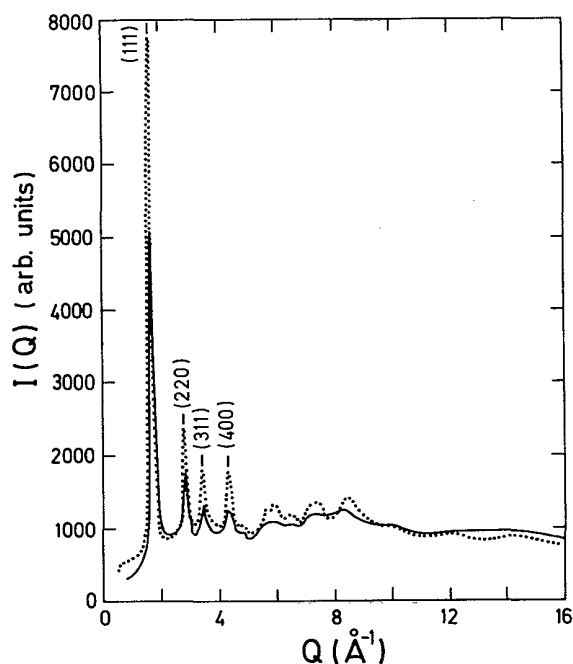


FIG. 5. Spectrum of cubic ice ($-198\text{ }^{\circ}\text{C}$) (dotted line) (Ref. 20) compared with that of confined D_2O at $-100\text{ }^{\circ}\text{C}$ from fully hydrated Vycor (full line).

long hexagonal channels extending all the way from the top to bottom. In case of cubic ice, the second plane of oxygen atoms is rotated around by 120° with respect to the first, this gives rise to a staggered arrangement. In Vycor we see Bragg peaks mainly due to cubic ice, perhaps because the confining geometry of the system would be less favorable to formation of long orderly hexagonal channels which accompany the formation of hexagonal ice.²³ Thus, the convoluted hydrophilic surface of silica²⁴ provides enough nucleation sites for the water molecules, i.e., to form the cubic ice phase and hence we see more nucleation of ice than in bulk water where such sites do not exist. However, the extent of supercooling can be still more inside some pores of Vycor than in bulk. In Fig. 6, we show a spectrum which gives a clear evidence of water which is present below the Bragg peaks at $-18\text{ }^{\circ}\text{C}$ obtained by subtraction of the weighted spectrum of the same sample cooled down to $-100\text{ }^{\circ}\text{C}$. Due to the small amount of liquid water ($\sim 23\%$), the statistics of the spectrum of confined water is poor and this makes the comparison with bulk water at the same temperature difficult. Traces of water are still present at $-41.5\text{ }^{\circ}\text{C}$ [Figs. 7(a) and 7(b)] in both fully and partially hydrated samples, though the amount of water in partially hydrated sample is much more than in fully hydrated sample at this temperature. On heating the full hydrated sample from $-100\text{ }^{\circ}\text{C}$ up to $4\text{ }^{\circ}\text{C}$ rapid neutron scattering scans show that the cubic ice I_c reverts into hexagonal ice I_h just before the liquid phase appears. That is in good agreement with previous observations by heating high density amorphous ice²⁴ or water contained in polyHEMA.¹⁰

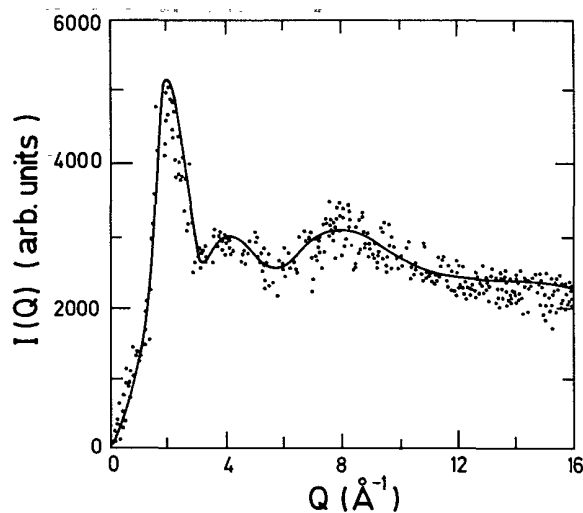


FIG. 6. Spectrum of confined D_2O at $-18\text{ }^{\circ}\text{C}$ from fully hydrated Vycor. This curve at $-18\text{ }^{\circ}\text{C}$ is obtained after subtraction of the weighted spectrum of the same sample cooled down to $-100\text{ }^{\circ}\text{C}$. There is $\sim 23\%$ liquid water.

B. Isochoric temperature derivative

To use this method, we assume that the variation of the density vs temperature, in confined water,²⁵ is the same as that in bulk water. For fully hydrated sample, we have considered two pairs of temperature ($-2.5, 26.8\text{ }^{\circ}\text{C}$) and ($-8, 34.4\text{ }^{\circ}\text{C}$). In Fig. 8, we compare the $\Delta d_L(r, \Delta T)/\Delta T$ results for confined water with those of bulk water¹³ for about the same pairs of temperature. In case of bulk water, the curves corresponding to the two temperature pairs can be superimposed except for the first peak near $2\text{ }^{\circ}\text{Å}$. This suggests that there is a universal ITD curve which effectively defines the structural changes over the $2\text{--}10\text{ }^{\circ}\text{Å}$ region. The small change in the composite peak at $\sim 2\text{ }^{\circ}\text{Å}$ for the higher ΔT value can be interpreted in terms of a saturation effect in the local hydrogen bonding interactions and the fourfold coordination occurring in the crystalline and amorphous forms of ice.

In case of confined water, the main changes occur between 2 and $16\text{ }^{\circ}\text{Å}$, opposite to that of bulk water. The observed effects can be understood in terms of increased orientational correlations mainly between 3 and $10\text{ }^{\circ}\text{Å}$ for the higher ΔT value.

V. CONCLUSION

It appears that the confining walls play an important role in modifying thermodynamic fluctuations in the liquid. In confined water we observe a small amount of unfreezable liquid at low temperature when compared to bulk water ($-31.5\text{ }^{\circ}\text{C}$) (Ref. 18), but there is a greater extent of nucleation of the ice which is the I_c cubic phase, instead of I_h hexagonal ice, and which is due to interaction with silica surfaces. The amount of supercooling of water in partially hydrated samples is much more than observed in

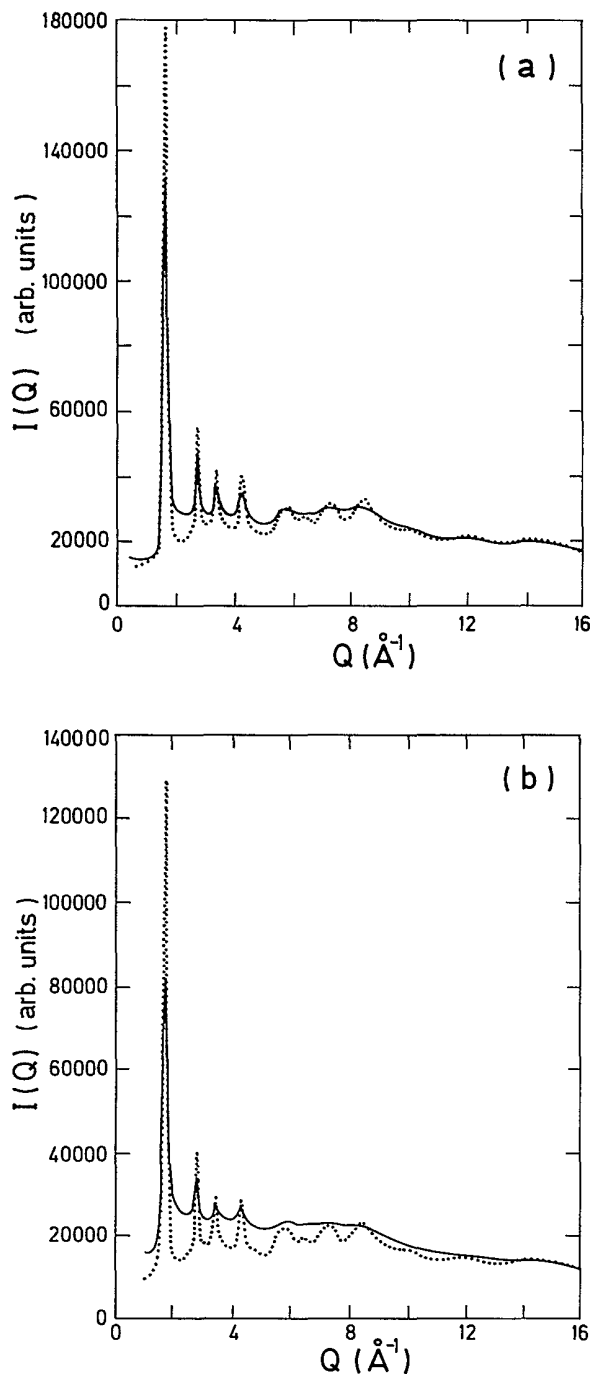


FIG. 7. (a) Spectra of cubic ice (dotted line) (-198°C) (Ref. 20) and confined D_2O from fully hydrated Vycor (full line) at -41.5°C ; there is $\sim 27\%$ liquid water still present below the Bragg peaks of cubic ice. (b) Spectra of cubic ice (dotted line) (-198°C) (Ref. 20) and confined D_2O from partially hydrated Vycor (full line) at -41.5°C ; there is $\sim 36\%$ liquid water still present below the Bragg peaks of cubic ice.

fully hydrated samples. The structure of confined water at 27°C looks very similar to that of bulk water at the same temperature.

We gave here the first detailed results about the structure of water at interfaces, using neutron scattering. But in order to improve our knowledge about water at hydro-

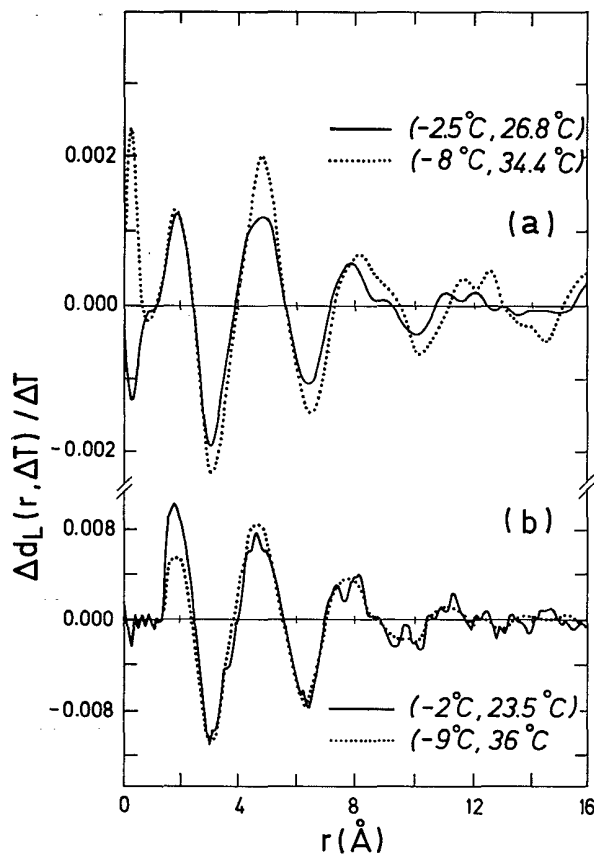


FIG. 8. Real-space distribution functions $\Delta d_L(r, \Delta T) / \Delta T$ for isochoric temperature derivative for the pairs of temperature (a) [-2.5°C , 26.8°C] and [-8°C , 34.4°C] for confined D_2O from fully hydrated Vycor compared with that of bulk water (b) for the pairs of temperatures [-2°C , 23.5°C] and [-9°C , 36°C] (Ref. 13).

philic interfaces, it is necessary to perform new experiments at even lower levels of hydration. Also, computer molecular dynamics simulations need to be done. Moreover, recently, the diffusional behavior of water molecules inside Vycor samples has been investigated by quasielastic neutron scattering, for the same levels of hydration of Vycor and the results will be reported later.

- ¹D. C. Steytler and J. C. Dore, *J. Phys. Chem.* **87**, 2458 (1983).
- ²D. C. Steytler, J. C. Dore, and C. J. Wright, *Mol. Phys.* **48**, 1031 (1983).
- ³D. C. Steytler and J. C. Dore, *Mol. Phys.* **5**, 1001 (1985).
- ⁴J. C. Dore, M. Dunn, and P. Chieux, *J. Phys. (Paris)* **48**, C1 (1987).
- ⁵J. C. Dore, F. Coveney, and M.-C. Bellissent-Funel, *Recent Developments in the Physics of Fluids*, edited by W. S. Howells and A. K. Soper (Adam Hilger, Bristol, 1992), p. 299.
- ⁶M. J. Benham, J. C. Cook, J. C. Li, D. K. Ross, P. L. Hall, and B. Sarkissian, *Phys. Rev. B* **39**, 633 (1989).
- ⁷R. K. Hawkins and P. A. Egelstaff, *Clays Clay Miner.* **28**, 19 (1980).
- ⁸A. K. Soper, *Hydrogen-Bonded Liquids*, edited by J. C. Dore and J. Teixeira (Kluwer Academic, Dordrecht, 1991), Vol. 329, p. 147.
- ⁹P. M. Wiggins, *Prog. Polym. Sci.* **13**, 1 (1988).
- ¹⁰L. Bosio, G. P. Johari, M. Oumezzine, and J. Teixeira, *Chem. Phys. Lett.* **188**, 113 (1992).
- ¹¹J. C. Dore, *Water Science Reviews 1-92*, edited by F. Franks (Cambridge University, Cambridge, 1985).
- ¹²G. Walford and J. C. Dore, *Mol. Phys.* **34**, 21 (1977).
- ¹³M.-C. Bellissent-Funel, *Hydrogen-Bonded Liquids*, edited by J. C. Dore

- and J. Teixeira (Kluwer Academic, Dordrecht, 1991), p. 117.
- ¹⁴P. A. Egelstaff, J. A. Polo, J. H. Root, L. J. Hahn, and S. H. Chen, *Phys. Rev. Lett.* **47**, 1733 (1981).
- ¹⁵General Information on Vycor Brand Porous "Thirsty" Glass, No. 7930, Corning Glass Works, is available from OEM Sales Service, Box 5000, Corning, New York 14830.
- ¹⁶G. K. Kennie and J. Clifford, *J. Chem. Soc. Faraday Trans.* **73**, 680 (1977).
- ¹⁷H. H. Paalman and C. J. Pings, *J. Appl. Phys.* **39**, 2635 (1962).
- ¹⁸M.-C. Bellissent-Funel, L. Bosio, and J. Teixeira, *J. Phys. Condensed Matter* **3**, 4065 (1991).
- ¹⁹M.-C. Bellissent-Funel, J. Teixeira, L. Bosio, and J. C. Dore, *J. Phys. Condensed Matter* **1**, 7123 (1989).
- ²⁰M.-C. Bellissent-Funel, L. Bosio, A. Hallbrucker, E. Mayer, and R. Sridi-Dorbez, *J. Chem. Phys.* **97**, 1282 (1992).
- ²¹L. Bosio, G. P. Johari, and J. Teixeira, *Phys. Rev. Lett.* **56**, 460 (1986); M.-C. Bellissent-Funel, J. Teixeira, and L. Bosio, *J. Chem. Phys.* **87**, 2231 (1987).
- ²²H. Savage, *Water Structure in Crystalline Solids: Ice to Proteins. Water Science Reviews*, edited by F. Franks (Cambridge University, Cambridge, 1986), Vol. 2, p. 67.
- ²³P. Chieux (private communication).
- ²⁴R. K. Iler, *The Chemistry of Silica* (Wiley, New York, 1979), Chap. 6, p. 622.
- ²⁵G. S. Kell, *J. Chem. Eng. Data* **20**, 97 (1975).