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Supplementary Information

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Ice crystallization observed in highly supercooled confined water †

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1 Analysis of the silica (10) Bragg peak

After normalization of the intensity of each diffraction pattern to its maximum, the *Q*-region from the onset of the Bragg peak, around Q = 0.2 Å⁻¹, downward has been fitted by a power law decay, $I(Q) = AQ^p$, as shown in Figure S1, and following the same procedure as in ¹. For each temperature the best fit yields an exponent close to -4, ($p = -4.13 \pm 0.14$). This result is in good agreement with the fractal dimension, F = 2, expected for a smooth surface². Since the fit parameters are weakly dependent on temperature, we subtracted the same background from the diffraction patterns collected at all temperatures probed, and the result is shown in fig. 2 of the main manuscript.

Previous SANS studies on water confined in MCM-41^{1,3,4}, considered the presence of a minimum in the intensity of the Bragg peak on cooling as directly related to the presence of a minimum in density of the confined liquid. Reasons behind this statement become clear if we explicitly write the model describing the measured scattered intensity in the *Q*-range between 0.1 and 0.3 Å⁻¹. This latter quantity can be written as:

$$I(Q) = nV_p^2(\Delta \rho)^2 \bar{P}(Q)S(Q)$$
(1)

where *n* is the number of scattering units (i.e. water cylinders) per unit volume, V_p is the volume of a single scattering unit, $\Delta \rho = \rho_{D_2O} - \rho_{MCM}$ is the neutron contrast, i.e. the difference of the



Fig. 1 Color Online. Background at low Q, $I(Q) = AQ^p$, with p < 0, for each DCS obtained from MCM-41/C10-D₂O-hydrated sample. Each curve represents the experimental diffraction pattern at different temperatures, whereas the black line (in log-log scale) indicates the power law fit function with $p = -4.13 \pm 0.14$.

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coherent scattering length density between heavy water and the MCM matrix, $\overline{P}(Q)$ is the normalized form structure factor of the scattering unit, and S(Q) is the interparticle structure factor of a 2D hexagonal lattice. It should be noted that the scattering geometry (an array of long cylinders with a small circular cross section, as in the case of the MCM-41 matrix) essentially selects only those cylinders whose axis is perpendicular to the change in momentum vector, Q. As a result the scattering data in the region of the (10) Bragg peak are relatively insensitive to the variation in scattering density along the cylinders' axes.

Since the thermal expansivity of the silica substrate is negligible compared to that of water in this temperature range, eq. 1 tells us that the scattering intensity is proportional to the square of $\Delta \rho$. This latter term contains the *contrast* contribution to the scattered intensity. In particular, $\rho_{D_2O} = \alpha \rho_m$ is proportional to the mass density, ρ_m , of D₂O, with $\alpha = (N_A \sum b_j)/M$ and where N_A is the Avogadro's number, *M* the D₂O molecular mass, and b_j the coherent scattering length of the *i*-th atom in the scattering unit.

The form structure factor $\overline{P}(Q)$ of a long cylinder is given by⁵:

$$\bar{P}(Q) = \frac{\pi}{QL} \left(\frac{2J_1(QR)}{QR}\right)^2 \tag{2}$$

where *L* and *R* are the length and radius of the cylinder, respectively (with $QL \ge 2\pi$), and $J_1(x)$ is the first-order Bessel function of the first kind. Finally, the interparticle structure factor S(Q) of a perfect 2D hexagonal lattice is a series of Delta functions (Bragg peaks) located at $Q_1 = 2\pi/a$, $Q_2 = 2\sqrt{3}\pi/a$,..., where *a* is the length of the primitive lattice vector of the hexagonal array of cilynders. In this case we have to take into account the unavoidable broadening of the Bragg peaks due to defects in the real lattice and the finite size of the grains. As a result, the structure factor S(Q) can be well approximated by a Lorentzian function. Summarizing, the measured neutron scattering intensity after background subtraction can be expressed as:

$$I(Q) = nV_p^2 (\alpha \rho_m - \rho_{MCM})^2 \frac{\pi}{QL} \left(\frac{2J_1(QR)}{QR}\right)^2 \left(\frac{\frac{1}{2}\Gamma}{(Q-Q_0)^2 + (\frac{1}{2}\Gamma)^2}\right)$$
(3)

where Q_0 is the Bragg peak position. In the latter equation all the variables are independent of temperature, except for ρ_m , the mass density of confined water. On the basis of this observation, it is therefore possible to determine the density of confined D₂O by measuring the temperature-dependent neutron scattering intensity of the Bragg peak at Q = 0.2 Å^{-11,4}, assuming that ρ_m is constant across the pore. We have fitted the model described above to our diffraction data (after the background subtraction), rewriting eq. 3 in a simpler form:

$$I(Q) = C \frac{J_1(QR)^2}{Q^3 R^2} \left(\frac{\frac{1}{2}\Gamma}{(Q - Q_0)^2 + (\frac{1}{2}\Gamma)^2} \right)$$
(4)

with the pre-factor

$$C = I(Q_0) = A(\rho_m - C_0)^2$$
 (5)

The temperature-independent parameter C_0 , related to the



Fig. 2 Color Online. Freezing point depression of heavy water confined in MCM-41 matrix (Figure adapted from Ref. ¹²). The plot shows the depression of the freezing temperature, ΔT_p , in confined water as a function of the inverse pore radius ($R' = R - \lambda$), where λ is the thickness of a nonfreezable interfacial water layer. The solid line is the best fit of the data, and its parameters have been used to calculate the constant C_{GT} in the modified Gibbs-Thomson equation.

scattering length density of the silica matrix, has been estimated applying the same fitting function (eq. 4) to the diffraction pattern obtained from the MCM sample filled with the "zero-water" mixture at ambient temperature. The neutron scattering length of this mixture, made up of 92% H_2O and 8% D_2O , is such that the average coherent scattering length of the water molecule as a whole is zero, so that structural signal from confined water is suppressed and only the contribution from the confining matrix is visible.

The constant *A* in eq. 5 was determined as follows. In analogy with ^{1,3,6,7}, we normalized the density obtained at the highest temperature to that of bulk D_2O at ambient pressure (1.11 g/cm³) taken from NIST Standards⁸. Even though it is well known that the density of confined water is significantly lower than its bulk density, as shown in ^{9–11}, this normalization makes it possible to compare the present data with those published in Ref.¹.

Thickness of the unfreezable water layer

The parameter λ , appearing in a modified form of the Gibbs-Thomson equation¹²:

$$\Delta T_p = \frac{C_{GT}}{R - \lambda} \tag{6}$$

represents the thickness of a non-freezable water layer at the pore walls. In the above equation, C_{GT} is a constant value¹². Figure S2 (adapted from¹²) shows the depression of melting/freezing point, ΔT_p , of D₂O for pores with different diameters in the range 2-10 nm, as a function of the inverse of $R' = R - \lambda$.

Using the data plotted in Fig. S2, we evaluated the value of the constant C_{GT} as the slope of ΔT_p vs $R' = R - \lambda$. We then made use of the experimental evidence of ice nucleation event as resulting from our neutron diffraction data ($\Delta T_p = 34$ K) and applied eq. 6 to obtain an estimate for $\lambda = R - (C_{GT}/\Delta T_p)$. The resulting value is $\lambda = 0.38$ nm.

As a side consideration, we suggest that the absence of DSC peaks, due to first-order phase transitions related to melting/freezing of water confined in pores with diameters $< 3 \text{ nm}^{13}$, could not be taken as evidence for the suppression of crystallization of confined water, but rather as an indication of an upper limit of experimental detectability. To support this suggestion, we notice that the onset of crystallization at 230 K we observed when water is confined in MCM-41/C18 corresponds to the freezing point depression measured by DSC, when water is confined in pores with a diameter of 4.5 nm (same as that of MCM-41/C18)¹².

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