

## Collective dynamics of supercooled water confined in MCM-41 porous silica by NSE

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In spite of a lot of theoretical and experimental studies of supercooled water, first-order liquid-liquid transition and the existence of the second low-temperature critical point of water are still controversial. The thermodynamic values and the transport properties of supercooled water show a divergence towards 228 K at the ambient pressure [1, 2]. However, there is no direct evidence of the first-order liquid-liquid transition because the second low-temperature critical point is expected to be in the so-called "no-man's land".

Confined water in nano-scale pore is appropriate to search the anomaly at low temperatures because we can easily reach supercooled condition there. Especially, in supercooled water confined in porous materials whose pore size is less than ~2.2 nm, the homogenous nucleation does not take place. So far, dynamics of water confined in Vycor glass was studied by neutron spin echo technique [3]. However, Vycor glass and molecular sieves are characterized by random orientations and a wide distribution of pore size. Micelle-templated mesoporous silica materials, such as MCM-41, have homogeneous 1D cylindrical pores characterized by a 2D hexagonal arrangement. Therefore, because the modeling of MCM-41 in computer simulation is easier than that of Vycor glass, the experimental results of water confined in MCM-41 can be more strictly compared with those of the corresponding computer simulations.

Recently, an incoherent quasi-elastic neutron scattering study has revealed a fragile to strong dynamic transition in supercooled water confined in MCM-41-S (pore size is 1.4 nm) from temperature and pressure dependence of average translational correlation times of water [4]. The investigation of such a slow dynamics is more preferable in time domain because the analysis of the peak shape strongly depends on convolution effects in the frequency domain. On the other hand, because neutron spin echo measurement gives the correlation function in the time domain directly, the resolution correction is easier than for the quasi-elastic neutron scattering. Moreover, collective dynamics by coherent neutron scattering is more sensitive to structure change of water than single particle motion. We have performed coherent neutron spin echo measurements of heavy water confined in MCM-41 C10 (pore size is 2.04 nm) in a temperature range from ambient temperature to 50K.

The prepared MCM-41 C10 samples were packed in a square flat aluminum cell (30×40×8 mm). Heavy water vapor was 3 times repeatedly contacted with the sample after evacuation and lastly adsorbed up to the capillary condensation at the humidity to fill the pores,  $P/P_0=0.55$ . After loading the pores with heavy water, the sample cell was filled with helium gas and sealed with indium wire and aluminum screws.

NSE measurements were made on the IN11C spectrometer at Institute Laue-Langevin (Grenoble, France) with an incident neutron wavelength of 0.8 nm. The instrument setup was tuned to  $Q$  range of 14 ~ 19 nm<sup>-1</sup> in order to cover the first peak in the static structure factor of water. The range of Fourier time was covered from 2 ps to 0.6 ns

Intermediate scattering functions (ISF) of heavy water adsorbed in MCM-41 C10 at 50, 200, 220, 240, 255, 270, and 290 K in the vicinity of the first peak at ~17 nm<sup>-1</sup> of  $S(Q)$  of heavy water are shown in Fig. 1. All ISFs were normalized by  $I(Q, 0)$  at  $t = 0$  and divided by ISF at 50 K, where the scattering is almost elastic because, at experimental resolution, any relaxation with long time scale of water is detectable. The ISF data were fitted with the Kohlrausch-Williams-Watts (KWW) stretched exponential function according to the relation: [5, 6]

$$I(Q,t) = (1 - p(Q))A(Q)\exp\left\{-\left(\frac{t}{\tau(Q)}\right)^{\beta(Q)}\right\} + p(Q) \quad (1)$$

where  $A(Q)$ ,  $\tau(Q)$ ,  $\beta(Q)$  and  $p(Q)$  indicate the Debye-Waller factor, relaxation time, stretched exponent, and elastic term attributed to silica, respectively. We identified a maximum in  $\tau(Q)$  at ~17 nm<sup>-1</sup> corresponding to the first diffraction peak of  $S(Q)$  for all temperatures. This feature was predicted by the mode coupling theory (MCT) for supercooled water [7].

There is no temperature dependence of  $A(Q)$ . The present  $\beta(Q)$  values coincide with those (0.66 – 0.80) obtained from our previous incoherent QENS measurements in MCM-41 C10 between 238 and 298 K [8]. These values are also similar to those of supercooled water in the bulk (0.62 – 0.56) [9]. There is no remarkable  $Q$  dependence in the values of  $\beta(Q)$  at 290 and 270 K. However, at 255 K and 240 K, we can find subtle maxima around 17 nm<sup>-1</sup> as predicted by the MCT [7]. This is explained in terms of the enhancement of the water cages due to the partially recovered tetrahedral-like structure at low temperatures [10]. The deviation of  $\beta(Q)$  from unity indicates that the relaxation time of water molecule has a wide distribution even at ambient conditions. The distribution becomes wider with decreasing temperature.

We estimated the glass transition parameters and the degree of fragility from temperature dependence of  $\tau(Q)$  by using the Vogel-Fulcher-Tammann (VFT) equation as follows:

$$\tau(Q) = \tau_0(Q)\exp\left(\frac{D(Q)T_0(Q)}{T - T_0(Q)}\right) \quad (2)$$

where  $\tau_0(Q)$  is the pre-exponential factor,  $D(Q)$  a constant providing the measure of fragility, and  $T_0(Q)$  the ideal glass transition temperature, respectively. Fig. 2 shows a typical fitting result of  $\tau(Q)$  at  $Q = 16.7$  nm<sup>-1</sup>. The temperature dependence of  $\tau(Q)$  values follows the VFT law in a temperature range from 290 down to 240 K; however, the values at 220 and 200 K deviate from the VFT curve. Similar trends for  $\tau(Q)$  are observed at other  $Q$  values. This implies that confined water is a fragile liquid up to 240 K. The transition point of fragile-to-strong of supercooled water has been found to be ~230 K that is by 5 K higher than that obtained by incoherent QENS studies [11]. In general, the fragility of liquids is characterized by some high non-Arrhenius behavior in the relaxation times [12]. In the case of water, the fragility is related to the degree of development of the tetrahedral-like network

structure. The present results show that in the temperature range of 240 - 290 K, even in the MCM-41 smaller pores (2.04 nm), the supercooled water has not fully developed a tetrahedral-like network structure and is a high-density liquid. At 200 and 220 K, we observed some departure from the VFT law where some trend to a fragile to strong liquid transition has been reported, which is in agreement with the results of interfacial water in Vycor [13], supercooled water in MCM-41-S [4], and those by MD simulation [14].

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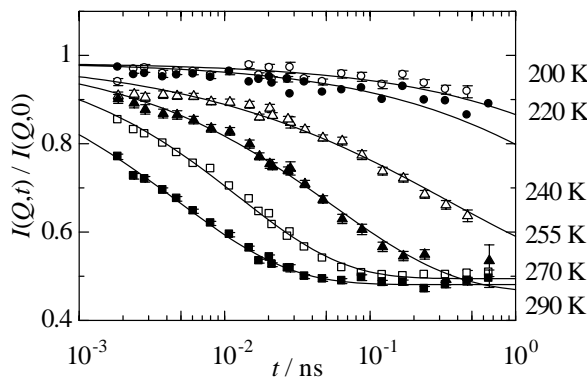


Fig. 1. Intermediate scattering functions (ISF) of heavy water adsorbed MCM-41 C10 at 200, 220, 240, 255, 270, and 290 K in the vicinity of the first peak at  $\sim 17 \text{ nm}^{-1}$  in  $S(Q)$  of heavy water.

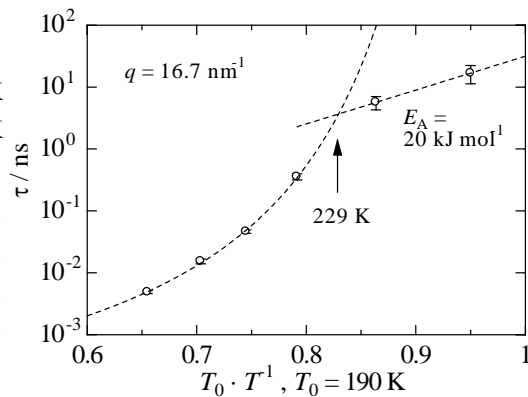


Fig. 2. Temperature dependence of the relaxation times  $\tau(Q)$  of heavy water confined in MCM-41 C10 at  $16.7 \text{ nm}^{-1}$ . The dashed line for  $T > 240 \text{ K}$  indicates the fit to the VFT law.