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## Dynamic crossover in deeply cooled water confined in MCM-41 at 4 kbar and its relation to the liquid-liquid transition hypothesis

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With quasi-elastic neutron scattering, we study the single-particle dynamics of the water confined in a hydrophilic silica material, MCM-41, at 4 kbar. A dynamic crossover phenomenon is observed at 219 K. We compare this dynamic crossover with the one observed at ambient pressure and find that (a) above the crossover temperature, the temperature dependence of the characteristic relaxation time at ambient pressure exhibits a more evident super-Arrhenius behavior than that at 4 kbar. Especially, at temperatures below about 230 K, the relaxation time at 4 kbar is even smaller than that at ambient pressure. This feature is different from many other liquids. (b) Below the crossover temperature, the Arrhenius behavior found at ambient pressure has a larger activation energy compared to the one found at 4 kbar. We ascribe the former to the difference between the local structure of the low-density liquid (LDL) phase and that of the high-density liquid (HDL) phase, and the latter to the difference between the strength of the hydrogen bond of the LDL and that of the HDL. Therefore, we conclude that the phenomena observed in this paper are consistent with the LDL-to-HDL liquidliquid transition hypothesis. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4930855]

#### I. INTRODUCTION

Water under strong confinement attracted a great deal of attention in recent years due to its unusual thermodynamic, dynamic, and structural properties at low temperatures. Particularly, the water confined in a hydrophilic matrix, MCM-41, has been extensively investigated.<sup>1</sup> MCM-41 is a mesoporous silica material that is composed of grains with the length scale of micrometer. In each grain, parallel and uniform sized cylindrical pores are arranged in an ordered two-dimensional hexagonal lattice (see Fig. 1(a)). Differential scanning calorimeter measurement shows that water can be kept in liquid state at least down to 130 K when confined in MCM-41 with the pore diameter smaller than 17 Å.<sup>2</sup> Note that this temperature is much lower than the bulk homogeneous nucleation temperature  $T_H$ (232 K at 1 atm), below which the bulk liquid water will crystallize inevitably. Therefore, the confined water system is very valuable for exploring the behaviors of liquid water at temperatures below  $T_H$ .

In 2004, Faraone et al. observed a dynamic crossover phenomenon at about 225 K in water confined in MCM-41 with quasi-elastic neutron scattering (QENS).<sup>3</sup> Its existence was confirmed by nuclear magnetic resonance technique.<sup>4</sup> The dynamic crossover refers to a phenomenon that the temperature dependence of the characteristic relaxation time of water transforms from a "fragile" behavior at high temperatures

to a "strong" behavior at low temperatures. The temperature at which the crossover takes place is called the crossover temperature  $(T_x)$ . The "fragile" behavior of the characteristic relaxation time is liquid-like and can be described by the Vogel-Fulcher-Tammann (VFT) law,

$$\langle \tau \rangle \propto \exp[DT_0/(T-T_0)],$$
 (1)

where  $\langle \tau \rangle$  is average characteristic relaxation time of water. D is a constant providing the measure of fragility.  $T_0$  is the ideal glass transition temperature. The "strong" behavior of the characteristic relaxation time is solid-like and can be described by the Arrhenius law,

$$\langle \tau \rangle \propto \exp(E_A/k_B T),$$
 (2)

where  $E_A$  is the activation energy and  $k_B$  is the Boltzmann constant. The dynamic crossover phenomenon observed in the confined water is similar to the "fragile-to-strong transition" of the structural relaxation process of water proposed by Ito et al.<sup>5</sup> According to this similarity, Faraone et al. ascribe this phenomenon to a qualitative change in the temperature dependence of the structural relaxation time of the confined water from "fragile" behavior to "strong" behavior as crossing  $T_x$  from above and name this phenomenon "fragile-to-strong crossover."3

Besides the dynamic crossover, another topic relevant to the confined water under active investigation is its phase behavior. Recently, with elastic neutron scattering, we measured the average density of the heavy water confined in

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FIG. 1. (a) The two-dimensional hexagonal pore structure of MCM-41 used in this study. The center-to-center distance between two adjacent pores is marked as "*a*", and the distance between two adjacent rows is marked as "*d*". (b) The phase diagram of the deeply cooled confined D<sub>2</sub>O determined with density measurement.<sup>8</sup> The black solid line denotes the liquid-liquid transition line and the green ellipse denotes the liquid-liquid critical point. The pink up triangles and blue down triangles denote the measured points at ambient pressure and at 4 kbar, respectively.

MCM-41 and found a likely high-density liquid (HDL) to lowdensity liquid (LDL) transition in the deeply cooled region of this system.<sup>6–8</sup> The phase diagram<sup>8</sup> is shown in Fig. 1(b). This result qualitatively agrees with the idea of the liquid-liquid phase transition in the liquid water predicted by a computer simulation study.<sup>9</sup>

The above two phenomena are believed to be closely related to each other.<sup>10–12</sup> With computer simulation, Xu *et al.* show that the Widom line of the liquid-liquid transition coincides with the loci of the "fragile-to-strong transition" in the pressure-temperature (P-T) plane.<sup>11</sup> Widom line is the extension of the first-order liquid-liquid transition line into the onephase region. It can be defined as the locus of the maximum of the isobaric heat capacity of water.<sup>11</sup> By crossing the Widom line temperature from above, water transforms from a HDLlike form to a LDL-like form. Liu et al. measure the "fragile-tostrong crossover" in the confined water at high pressures.<sup>10,13</sup> They find that below 1.4 kbar, the crossover temperature  $T_x$  decreases as the pressure increases. However, at pressures higher than 1.6 kbar, the crossover cannot be identified anymore. With the idea proposed by Xu et al., Liu et al. assign the positions at which the crossovers take place in the P-T plane to the locus of the Widom line in the confined water and ascribe the disappearance of the crossover at pressures higher than 1.6 kbar to the emergence of liquid-liquid phase separation.<sup>10</sup> The coincidence of the Widom line and the dynamic crossover in the confined water is supported by a Fourier transform infrared spectroscopic study. By investigating the vibrational spectra of the confined water, Mallamace et al. show that at  $T_x$ , the confined water is a mixture composed of 50% LDL

and 50% HDL, which is a feature of the Widom line.<sup>12</sup> Nevertheless, whether this crossover phenomenon observed in the confined water can mark the crossing of the Widom line is still in debate.<sup>14–17</sup> The major criticism is that the relaxation time obtained at temperatures below  $T_x$  in QENS study is not the structural or translational relaxation time of the system. Thus, the dynamic crossover observed in the confined water is different from the "fragile-to-strong transition" proposed by Ito *et al.* and cannot be ascribed to crossing the Widom line. In order to avoid confusion, in the following part, we will use the term "dynamic crossover" rather than "fragile-to-strong crossover" to denote this dynamic phenomenon.

Previous experimental studies on the single-particle dynamics of the confined water are up to 2.4 kbar.<sup>10,13</sup> In the view of above, it is necessary to have dynamic measurements at higher pressures. From the phase diagram shown in Fig. 1(b), one can find that at pressures higher than 3.5 kbar, the confined water is dominated by the HDL phase. According to a recent study,<sup>18</sup> HDL and LDL exhibit different glassy behaviors at low temperatures. Therefore, the study on the single-particle dynamics of the confined water at pressures higher than 3.5 kbar may provide useful information on the possible liquid-liquid transition in the confined water.

Notice that the idea of the liquid-liquid transition was proposed for bulk water. The properties of the confined water can suffer from constraints induced by the confinement.<sup>1,19,20</sup> Therefore, to what extent the confined water is similar to the bulk water is questionable. However, the confined water system is still of fundamental importance because it represents many biological and geological systems where water resides in nanopores or in the vicinity of hydrophilic surfaces.

#### **II. EXPERIMENTAL METHODS**

We perform a QENS experiment at the High-Flux Backscattering Spectrometer (HFBS)<sup>21</sup> at National Institute of Standards and Technology Center for Neutron Research (NCNR) on the water confined in MCM-41 at 4 kbar. We also measure the same confined water system at 1 bar for comparison. The average pore diameter of the MCM-41, determined by the Barrett-Joyner-Halenda method with nitrogen sorption isotherms, is 15 Å. The hydration level *h* of the sample, defined as g H<sub>2</sub>O/g dry MCM-41, is 0.45. The energy window for the data analysis is from -10 to  $10 \ \mu$ eV. The energy resolution of the instrument is 0.8  $\mu$ eV.

The normalized QENS spectra of the confined water,  $I_{\text{H}_2\text{O}}(E)$ , were fitted with the following equation:

$$I_{\rm H_{2}O}(E) = \{ p\delta(E) + (1-p) FT [F_s(t)] \} \otimes R(E), \quad (3)$$

where *FT* denotes a time Fourier transform, R(E) is the energy resolution function,  $\otimes$  is the convolution operator, and *p* is the elastic fraction. The existence of the elastic component is due to the confinement.<sup>22</sup>  $F_s(t)$  is the self-intermediate scattering function (SISF). For supercooled confined water,  $F_s(t)$  can be modeled by stretched exponential decay form,<sup>23</sup>

$$F_s(t) \approx \exp[-(t/\tau)^\beta],\tag{4}$$

where  $\tau$  is the characteristic relaxation time of the long-time relaxation and  $\beta$  is the stretching exponent. Notice that the



FIG. 2. Measured QENS spectra of the confined water system along with the corresponding calculated curves fitted by Eq. (3) at Q = 0.75 Å<sup>-1</sup>. Panels (a) and (b) show the measured spectra and the calculated curves in logarithmic scale for P = 1 bar and 4 kbar, respectively. Panel (c) shows the measured spectra and the calculated curves in linear scale for four specific conditions.

above approximation only considers the translational contribution; thus, it only works when Q is smaller than about 1 Å<sup>-1</sup> where the local motions are not significant.<sup>10,23</sup> The mean characteristic relaxation time  $\langle \tau \rangle$  is calculated from  $\tau$  and  $\beta$  by  $\langle \tau \rangle = \beta^{-1} \Gamma(\beta^{-1}) \tau$ . In this study,  $\beta$  is fixed to 0.5, which has been found to be the case in many neutron scattering studies on the confined water and interfacial water.<sup>24–27</sup> This value of stretching exponent fits the data well as can be seen in Fig. 2. The value of p was obtained from the fit of the spectrum at the highest measured temperature, since the elastic fraction p is most easily distinguished at the highest temperature.

#### **III. RESULTS AND DISCUSSION**

Figure 2 shows the measured spectra of the confined water system along with the corresponding calculated curves fitted by Eq. (3) at Q = 0.75 Å<sup>-1</sup>. Figures 3(a) and 3(b) show the Arrhenius plots of  $\langle \tau \rangle$  at Q = 0.75 Å<sup>-1</sup> for P = 1 bar and 4 kbar, respectively. In Fig. 3(a), the higher-temperature data exhibit super-Arrhenius behavior, which can be fitted by the VFT relation (Eq. (1)). The lower-temperature data exhibit Arrhenius behavior, which can be fitted by the Arrhenius relation (Eq. (2)). In this case, the crossing temperature of these two fits, i.e., the dynamic crossover temperature  $T_x$ , is 225 K, which is very close to the value obtained in previous studies, 224 K.<sup>10</sup> At 4 kbar, we also find a dynamic crossover, which takes place at 219 K. Note that there is no liquid-liquid transition or Widom line at such high pressure according to the phase diagram shown in Fig. 1(b). Nevertheless, this is not very unexpected because the dynamic crossover does not necessarily relate to a Widom line or a phase transition.<sup>28</sup> Since the relation between the Widom line and the dynamic crossover in the confined water is still in debate, in the following part, we will discuss our new result without assuming that the locus of the dynamic crossover coincides with the Widom line of the liquid-liquid transition.

From Fig. 3(c), one can find that at temperatures higher than  $T_x$ , the T dependence of  $\langle \tau \rangle$  at 1 bar exhibits a more evident super-Arrhenius feature than that at 4 kbar. Particularly, at temperatures below about 230 K, the relaxation time at 4 kbar is even smaller than that at 1 bar. This feature is guite unusual because for many other liquids, pressurizing leads to larger viscosities.<sup>29,30</sup> This point can also be seen in the measured spectra. From Fig. 2(c), it is found that at 266 K, the height of the measured spectrum at 1 bar is 0.023 67, which is slightly smaller than that at 4 kbar, 0.024 75. It indicates that at 266 K, the relaxation at 1 bar is a little faster than that at 4 kbar. However, this ordering reverses at lower temperatures. At 220 K, the height of the measured spectra at 1 bar is 0.090 44, which is considerably larger than the one at 4 kbar, 0.075 72. It shows that at 220 K, the relaxation at 1 bar is significantly slower than that at 4 kbar. The super-Arrhenius behavior of the confined water or interfacial water with sufficient hydration water is related to the collective relaxation process of water.<sup>24–26,31</sup> For a water molecule trapped in a cage consisting of its neighboring molecules, its translational diffusion requires cage breaking that is associated with simultaneous breaking of several hydrogen bonds. As T decreases, the local order surrounding a molecule is enhanced, which leads to a significant increase of the structural relaxation time.<sup>23</sup> Subsequently, this collective relaxation process exhibits a non-Arrhenius T dependence. For the case of P = 1 bar, as T decreases, the local structure of water gradually transforms from normal form to predominately LDL form.<sup>8,12</sup> The water molecule in the LDL phase has an open tetrahedral hydrogenbond network up to its second coordination shell.<sup>32</sup> Such a strong local order will weaken the fluidity of water molecule and lead to an evident super-Arrhenius behavior as temperature decreases. On the contrary, at 4 kbar, as T decreases, the local structure of water transforms to a HDL form.<sup>8</sup> A water molecule in the HDL phase only forms a tetrahedral hydrogenbond structure with its first coordination shell, while the second coordination shell collapses.<sup>32</sup> In this case, the enhancement of the local order as temperature decreases is not as strong as at 1 bar, which leads to a relatively weak super-Arrhenius behavior as temperature decreases and better fluidity of water molecule at low temperatures where the confined water is in a HDL-dominant form.

At temperatures lower than  $T_x$ , the activation energy  $E_a$  at 1 bar is 16.5 ± 3.9 kcal/mol, which is larger than the value obtained at 4 kbar, 13.9 ± 2.8 kcal/mol. This phenomenon suggests that the strength of the hydrogen bond in LDL is stronger than that in HDL. Recently, we measure the librational band in the vibrational density of state of the confined water.<sup>33</sup>



FIG. 3. Panels (a) and (b) show the Arrhenius plots of the mean characteristic relaxation time  $\langle \tau \rangle$  at 1 bar (red circles) and 4 kbar (black squares) at Q = 0.75 Å<sup>-1</sup>, respectively. The dynamic crossover takes place at 225 K in the former case and at 219 K in the latter case. We plot the above two results in panel (c). Note that at temperatures smaller than about 230 K, the  $\langle \tau \rangle$  at 4 kbar is smaller than that at 1 bar. Error bars throughout the paper represent one standard deviation.

It shows that the energy of the low-energy side of the librational band measured in the HDL is lower than that measured in LDL by a few meV. This spectral difference indicates that the hydrogen bond becomes weaker from LDL to HDL. Therefore, the decrease of the activation energy  $E_a$  from 1 bar to 4 kbar found in this study is consistent with the result of the measurement on the librational motion of the confined water molecule.

Figure 4 shows the positions of the dynamic crossovers in the *P*-*T* plane. As mentioned before, the dynamic crossover disappears at pressures higher than 1.6 kbar.<sup>10,13</sup> In this work, we show that the dynamic crossover reappears at 4 kbar. In addition, the position of the dynamic crossover at 4 kbar deviates from the extrapolation of the positions of  $T_x(P)$  below 1.6 kbar significantly. Both of these two phenomena indicate a discontinuity between 1.5 and 4 kbar. According to Fig. 1(b), there is a liquid-liquid transition between 1.3 and 3.5 kbar. For this consideration, it is reasonable to ascribe the discontinuous behavior of  $T_x(P)$  to the existence of the phase separation in the confined water.

In previous studies, we estimate the critical pressure of the confined water to be 1.6 kbar by the dynamic properties of the system, including the dynamic crossover<sup>10,13</sup> and the boson peak.<sup>34</sup> The critical pressure obtained by the density measurement is  $1.3 \pm 0.3$  kbar (see Fig. 1(b)), which is smaller than the former value. Note that the density measurement has a very

good signal-to-noise ratio;<sup>6,8</sup> thus, its result is quite sensitive to the phase separation. However, the dynamic properties are not so sensitive. The changes of the dynamic properties, such as the disappearance of the dynamic crossover, only appear when the phase separation is significant enough. Thus, it is not surprising that the critical pressure estimated by dynamic properties is



FIG. 4.  $T_x(P)$  in the *P*-*T* plane. The black squares represent the positions of the dynamic crossover observed by Liu *et al.*<sup>10,13</sup> The red circles represent the positions of the dynamic crossover observed in this study. Notice that according to Liu *et al.*,<sup>10,13</sup> the dynamic crossover disappears from 1.6 kbar to the highest pressure they measured, which is 2.4 kbar.

higher than that obtained from the density measurement with elastic neutron scattering.

#### **IV. CONCLUSION**

In this paper, we investigate the single-particle dynamics of the water confined in MCM-41 at 4 kbar with QENS. A dynamic crossover phenomenon is observed at 219 K. We compare this dynamic crossover and the one found at 1 bar and discuss the relation between these observations and the liquid-liquid transition hypothesis. Note that the discussions here do not rely on the controversial assumption that the dynamic crossover observed in the confined water coincides with the Widom line of the liquid-liquid transition. The two major points are summarized as follows.

- (a) Above the crossover temperature, the temperature dependence of the characteristic relaxation time at ambient pressure exhibits a more significant super-Arrhenius behavior than that at 4 kbar. Particularly, at temperatures below about 230 K, the relaxation time at 4 kbar is even smaller than that at 1 bar, which is different from many other liquids. In the viewpoint of liquid-liquid transition hypothesis, these observations are due to the difference in the local structures of LDL and HDL. LDL has a more ordered and open local structure, which leads to a more rapid increase in the relaxation time as temperature decreases at 1 bar. In contrast, HDL has a local structure that is not as open and ordered as that of LDL, which leads to a relatively weak super-Arrhenius behavior at 4 kbar.
- (b) Below the crossover temperature, the Arrhenius behavior found at ambient pressure has a larger activation energy compared to the one found at 4 kbar. We ascribe this observation to the decrease of the hydrogen-bond strength from LDL to HDL, as suggested by the inelastic neutron scattering measurement on the librational motion of the confined water molecule.<sup>33</sup>

In addition, we find that the pressure dependence of the crossover temperature suggests a discontinuity between 1.6 and 4 kbar, which corresponds to the likely liquid-liquid transition observed between 1.3 and 3.5 kbar in confined  $D_2O$  with elastic neutron scattering. For these reasons, we conclude that the phenomena observed in this paper are consistent with the liquid-liquid transition hypothesis.

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