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Abstract – Microscopic dynamics of water confined in nanometer and sub-nanometer pores of carbide-derived carbon (CDC) were investigated using quasielastic neutron scattering (QENS). The temperature dependence of the average relaxation time, \(\langle \tau \rangle\), exhibits super-Arrhenius behavior that could be described by Vogel-Fulcher-Tammann (VFT) law in the range from 250 K to 190 K; below this temperature, \(\langle \tau \rangle\) follows Arrhenius temperature dependence. The temperature of the dynamic crossover between the two regimes in water confined in the CDC pores is similar to that observed for water in hydrophobic confinement of the larger size, such as 14 \(\AA\) ordered mesoporous carbon (CMK) and 16 \(\AA\) double-wall carbon nanotubes. Thus, the dynamical behavior of water remains qualitatively unchanged even in the very small hydrophobic pores.

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Introduction. – The anomalous behavior of water in the supercooled state has triggered many investigations of its dynamical properties and has become one of the intriguing issues in the liquid-state physics in recent years [1–6]. Similar to the behavior observed in fragile glass-forming liquids, the structural relaxation in supercooled water exhibits non-Arrhenius temperature dependence. It has been speculated that the structural relaxation time of water might behave in a manner similar to other glass-forming liquids, where the non-Arrhenius behavior ceases and Arrhenius behavior emerges around a critical temperature, \(T_c\). Water is supposed to have a glass transition temperature \((T_g)\) at 165 K, hence the critical temperature is expected to be around 200 K \((T_c \approx 1.2T_g)\) [7]. Because of homogeneous nucleation in bulk water that starts at 235 K, reaching the supercooled state below 235 K is not possible. Confining water in mesopores allows supercooling water to much lower temperatures. For example, suppression of the melting/freezing transition down to temperatures as low as 206 K was reported for water confined in hydrophobic material with 2.3 nm pores [8]. There have been simulations and experiments demonstrating that, under nano-confinement (particularly, in carbon nanotubes [2,3,9]), freezing of water can be avoided altogether; in fact, water has been found to undergo transformation into glassy state. This provides an opportunity for investigating the dynamics of confined, albeit not bulk-like, water in deeply supercooled state.

Apart from the fundamental understanding of dynamics in nano-confinement, investigation of fluids in nano-confinement is of considerable technological importance. For example, it was demonstrated recently that carbon-based electrical double-layer capacitors that utilize electrolyte liquids confined in nanopores with a pore size less than the solvated shell size (10–15 \(\AA\)) show a tremendous increase in capacitance [10]. This enhancement may come along with substantial retardation of ion motions and diminished permittivity in pores less than the size of the ion. The solvation shell becomes highly distorted as the ion is squeezed through the pore [11]. The maximum capacitance was observed for pores of about 10 \(\AA\) in diameter, when an aqueous electrolyte was used [12]. In a molecular-dynamics simulation study it was also suggested that the dynamics of water become enhanced when water is confined in a hydrophobic channel of a carbon nanotube with a diameter less than 10 \(\AA\) [13]. However, the microscopic dynamics of water in carbon pores with size smaller than 10 \(\AA\) has not been investigated experimentally. It is

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distributions can be found in [14], and CO both samples [15]. Adsorption isotherms and pore size confirmed that pores were completely filled with water in 600 and CDC-800, respectively. SANS experiments also and 10 dry and wet CDC powders. The intake of H2 were calculated from the weight difference between the room temperature in the same furnace. Hydration levels scissoring temperature; details have been reported elsewhere [14]. The pore size distribution in these samples has been studied using gas sorption and small-angle neutron scattering (SANS) [15]. The pores were found to be cylindrical in shape, with 6.1 ± 1.1 Å and 7.8 ± 1.6 Å diameter and 10.20 ± 2.33 Å and 14.17 ± 2.18 Å length for CDC-600 and CDC-800, respectively. SANS experiments also confirmed that pores were completely filled with water in both samples [15]. Ar sorption isotherms and pore size distributions can be found in [14], and CO2 and N2 sorption data are available in [14]. There are only nanopores in both samples, no pores larger than 2 nm were found. The sample produced at 600 °C has only sub-nanometer pores, while the sample produced at 800 °C may have up to 20% pores (the exact number depends on the method used) in the 1–2 nm range. Water was confined in CDC powders with two different pore sizes, CDC-600 and CDC-800 (samples produced at 600 and 800 °C, respectively). Pure H2O was drawn into CDC pore by exposing CDC powders to saturated H2O vapors in a closed oven at 80 °C for 24 hrs. The samples were then cooled down to room temperature in the same furnace. Hydration levels were calculated from the weight difference between the dry and wet CDC powders. The intake of H2O per 1 g of CDC-600 and CDC-800 powders was 0.27 g and 0.31 g, respectively. QENS experiments were carried out on the new backscattering spectrometer (BASIS) at the Spallation Neutron Source, Oak Ridge National Laboratory. The analyzer wavelength, energy resolution at the elastic line (full width at half-maximum), and the Q range for the experiments were 6.267 Å, 3.4 μeV and 0.2 Å−1 to 2.0 Å−1, respectively. The thickness of the hydrated samples in the sample holders was chosen to ensure greater than 90% neutron beam transmission through the samples. To make sure that there was no bulk water present in our samples and to determine the temperature region suitable for the further investigation, we performed a short “elastic intensity scan” measurement. The elastically scattered neutrons were recorded with 5 K increments while cooling down the sample at a rate of 0.2 K/min in a temperature range of 300 K to 10 K. It is known that, if the confining pore size is significantly large, the confined water exhibits freezing transition, albeit at a much depressed temperature compared to 273 K, which, in a scattering experiment, manifests itself in an abrupt change in the elastic intensity at the transition temperature [16]. The transition temperature depends on the character of the pore walls (hydrophilic or hydrophobic) [8]. Within each series, hydrophobic and hydrophilic, the freezing temperature of confined water depends on the pore size [8]. For example, in hydrophilic silicate glasses with the large average pore size of 117 Å and 29 Å, the freezing temperatures were found to be at 262.4 K and 223.6 K, respectively [9]. In hydrophilic silica with smaller nanopores, the freezing transition was not observed down to at least 160 K when the pore size became 18 Å or smaller [6]. In our elastic intensity scans, there was no abrupt change either around freezing temperature of bulk water of 273 K, or at any lower temperatures. This suggests that in our samples there was neither bulk water, nor water in pores larger than approximately 18 Å, if any such larger pores were present (no such pores were expected [14]). The QENS experiments were carried out in a temperature range from 250 K down to 170 K with 10 K increments. Thus, our measurements were performed on supercooled confined water, above the glass transition temperature. For the resolution function, the data collected at 4 K were used. The temperature of the samples was controlled within ± 1 K and the QENS data were collected for about four hours at each temperature. The scattering intensity from our samples was mainly due to the large incoherent scattering from hydrogen atoms of confined water. Hence, the dynamics that we measure represent the single-particle motion of water molecules inside the carbon pores.

**Experiments.** – Nanoporous CDC powders [14] with a particle size of ~2 μm were used as the confining substrate. The pore size of the CDC was controlled by chlorination temperature; details have been reported elsewhere [14]. The pore size distribution in these samples has been studied using gas sorption and small-angle neutron scattering (SANS) [15]. The pores were found to be cylindrical in shape, with 6.1 ± 1.1 Å and 7.8 ± 1.6 Å diameter and 10.20 ± 2.33 Å and 14.17 ± 2.18 Å length for CDC-600 and CDC-800, respectively. SANS experiments also confirmed that pores were completely filled with water in both samples [15]. Ar sorption isotherms and pore size distributions can be found in [14], and CO2 and N2 sorption data are available in [14]. There are only nanopores in both samples, no pores larger than 2 nm were found. The sample produced at 600 °C has only sub-nanometer pores, while the sample produced at 800 °C may have up to 20% pores (the exact number depends on the method used) in the 1–2 nm range. Water was confined in CDC powders with two different pore sizes, CDC-600 and CDC-800 (samples produced at 600 and 800 °C, respectively). Pure H2O was drawn into CDC pore by exposing CDC powders to saturated H2O vapors in a closed oven at 80 °C for 24 hrs. The samples were then cooled down to room temperature in the same furnace. Hydration levels were calculated from the weight difference between the dry and wet CDC powders. The intake of H2O per 1 g of CDC-600 and CDC-800 powders was 0.27 g and 0.31 g, respectively. QENS experiments were carried out on the new backscattering spectrometer (BASIS) at the Spallation Neutron Source, Oak Ridge National Laboratory. The analyzer wavelength, energy resolution at the elastic line (full width at half-maximum), and the Q range for the experiments were 6.267 Å, 3.4 μeV and 0.2 Å−1 to 2.0 Å−1, respectively. The thickness of the hydrated samples in the sample holders was chosen to ensure greater than 90% neutron beam transmission through the samples. To make sure that there was no bulk water present in our samples and to determine the temperature region suitable for the further investigation, we performed a short “elastic intensity scan” measurement. The elastically scattered neutrons were recorded with 5 K increments while cooling down the sample at a rate of 0.2 K/min in a temperature range of 300 K to 10 K. It is known that, if the confining pore size is sufficiently large, the confined water exhibits freezing transition, albeit at a much depressed temperature compared to 273 K, which, in a scattering experiment, manifests itself in an abrupt change in the elastic intensity at the transition temperature [16]. The transition temperature depends on the character of the pore walls (hydrophilic or hydrophobic) [8]. Within each series, hydrophobic and hydrophilic, the freezing temperature of confined water depends on the pore size [8]. For example, in hydrophilic silicate glasses with the large average pore size of 117 Å and 29 Å, the freezing temperatures were found to be at 262.4 K and 223.6 K, respectively [9]. In hydrophilic silica with smaller nanopores, the freezing transition was not observed down to at least 160 K when the pore size became 18 Å or smaller [6]. In our elastic intensity scans, there was no abrupt change either around freezing temperature of bulk water of 273 K, or at any lower temperatures. This suggests that in our samples there was neither bulk water, nor water in pores larger than approximately 18 Å, if any such larger pores were present (no such pores were expected [14]). The QENS experiments were carried out in a temperature range from 250 K down to 170 K with 10 K increments. Thus, our measurements were performed on supercooled confined water, above the glass transition temperature. For the resolution function, the data collected at 4 K were used. The temperature of the samples was controlled within ± 1 K and the QENS data were collected for about four hours at each temperature. The scattering intensity from our samples was mainly due to the large incoherent scattering from hydrogen atoms of confined water. Hence, the dynamics that we measure represent the single-particle motion of water molecules inside the carbon pores.

**Result and discussion.** – In this report we analyze only the translational motion of water molecules in the CDC pores. At higher Q values (> 1.2 Å−1), there is a significant contribution to the scattering intensity due to the rotational motions of water molecules [5,17]. Thus, our QENS data analysis was limited to the Q values less than 1.2 Å−1. Figure 1 shows the fits of the scattering intensities using the model function described below. The elastic contribution is from the species that are not mobile within the resolution of the spectrometer. At higher temperatures, the quasielastic contribution grows in strength and its line width broadens because of the increasing mobility of the H2O molecules. To separate the elastic component from quasielastic contribution, the data were fitted with a function that includes elastic and quasielastic terms convoluted with the instrumental resolution function obtained at 4 K. The spectra obtained at each temperature and Q value were fitted independently using the following expression:

\[
S(E) = [x \delta(E) + (1 - x) S_{\text{QENS}}(E)] + B(E) + C \otimes R(E).
\]  

(1)

The \(\delta(E)\) is a delta function centered at zero energy transfer, \(x\) represents the fraction of elastic scattering, \(R(E)\) is the resolution function and \(B(E)\) is the background term of the form \(B(E) = B_1 + B_2/(E + E_0)^{-1}\), where \(E_0\) is the...
Quasielastic neutron scattering study of water confined in carbon nanopores

Fig. 1: (Color online) The scattering intensities from water confined in CDC nanopores (CDC-800, produced at 800°C). The solid squares are the data points and the solid line is the fit with eqs. (1) and (2). The short-dashed lines represent the quasielastic contribution (the Fourier-transformed stretched exponential relaxation function) and the long-dashed line is the instrument resolution spectrum measured at 4 K. Both lines are shifted down one and two orders of magnitude, respectively, for clarity. Also presented on the bottom of the graphs are the difference plots between the data and fits (not shifted with respect to the data and fits, to give the correct impression of the fits quality).

Elastic energy (2082 μeV). The model scattering function, $S_{QENS}(E)$ is the Fourier transformed stretched exponential relaxation function in the time space:

$$S_{QENS}(E) = A \int_0^\infty \exp \left[ -\left( \frac{t}{\tau} \right)^\beta \right] \exp \left( \frac{iE}{\hbar}t \right) dt,$$

where $A$ is a scaling constant, and $\beta (0 < \beta < 1)$ is the stretching parameter. We have not applied constraints to any parameter. The fit describes the data very well. From the fit parameters $\tau$ and $\beta$, the average relaxation times $\langle \tau \rangle$ were calculated as $[(\tau/\beta)\Gamma(1/\beta)]$, where $\Gamma$ is the Gamma function. We did not observe any systematic variation of the values for $\beta$ with $Q$ or temperature. The values of $\beta$ were within the range of 0.64 ± 0.12 for sample 1 and 0.88 ± 0.11 for sample 2. In fig. 2, the average relaxation times $\langle \tau \rangle$ are plotted as a function of inverse temperature for $Q$ values 0.5 Å$^{-1}$, 0.7 Å$^{-1}$, 0.9 Å$^{-1}$, and 1.1 Å$^{-1}$ for both samples. The values of $\langle \tau \rangle$ exhibit non-Arrhenius temperature dependence down to 190 K. At lower temperatures, they follow Arrhenius temperature dependence. Super-Arrhenius growth of the $\langle \tau \rangle$ values with decreasing temperature is a signature of alpha-relaxation, or long-range molecular motions. The $\langle \tau \rangle$ values between 250 K to 190 K are fitted with a Vogel-Fulcher-Tammann (VFT) law, $\tau = \tau_0 \exp[D(T - T_0)/T]$ where $D$ is the fragility parameter, $T_0$ is the ideal glass transition temperature and $\tau_0$ is the pre-factor. Below 190 K, $\langle \tau \rangle$ does not obey the VFT law; instead, the data can be well described using an Arrhenius temperature dependence; $\tau = \tau_1 \exp(E_A/RT)$, with an activation energy $E_A$; $R$ is the universal gas constant. There is a clear crossover observed at 190 K for both samples and for all $Q$ values investigated. The ideal glass transition temperature obtained from the VFT fits for sample 2 was similar to that obtained in QENS studies of water confined in 14 Å diameter single-wall, 16 Å diameter double-wall carbon nanotubes [2,3] and MCM-41 mesoporous silica [4]. The $T_0$ values tend to be lower for
Table 1: The pre-factor $\tau_0$, the ideal glass transition temperature $T_0$, fragility parameter $D$, from VFT fit and pre-factor $\tau_0$ and activation energy $E_A$ from Arrhenius fit to the temperature-dependent mean relaxation times.

<table>
<thead>
<tr>
<th>$Q$(Å$^{-1}$)</th>
<th>CDC-600 (produced at 600° C)</th>
<th>CDC-800 (produced at 800° C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VFT-Fulcher-Tammann</td>
<td>Arrhenius</td>
</tr>
<tr>
<td>$\tau_0$ (ps)</td>
<td>$T_0$ (K)</td>
<td>$D$</td>
</tr>
<tr>
<td>0.5</td>
<td>4.1 ± 1.7 × 10$^{-5}$</td>
<td>124</td>
</tr>
<tr>
<td>0.7</td>
<td>1.5 ± 0.1 × 10$^{-2}$</td>
<td>135</td>
</tr>
<tr>
<td>0.9</td>
<td>1.8 ± 0.3 × 10$^{-2}$</td>
<td>146</td>
</tr>
<tr>
<td>1.1</td>
<td>10.0 ± 0.9 × 10$^{-2}$</td>
<td>153</td>
</tr>
</tbody>
</table>

Fig. 2: (Color online) The average relaxation times of water molecules confined in CDC pores obtained for different $Q$ values: (left) CDC-600 and (right) CDC-800. A crossover between non-Arrhenius and Arrhenius temperature dependence occurs at about 190 K. The dashed lines are the fits with Vogel-Fulcher-Tammann equation ($\tau = \tau_0 \exp(DT_0/(T - T_0))$) (for temperatures 190 K–250 K) and the dotted lines are the fits with Arrhenius law ($\tau = \tau_0 \exp(E_A/RT)$) in the temperature range from 170 K to 190 K.

The choice of the modeling scattering function in the form of a Fourier-transformed stretched exponential is not unique. While the stretched exponential relaxation function can generally describe a dynamic process with a distribution of relaxation times, for confined supercooled water it has been associated with the relaxing cage model. The stretched exponential relaxation function that we used yields good-quality fits, yet the question is: how justified is its use for water confined in such small pores? A recent study of water on nanopowder oxide surfaces showed that the development of super-Arrhenius relaxation dynamics requires the amount of water just in excess of one mobile hydration layer. That is, a system of just two layers of water molecules already exhibits “bulk-like” caging effect. Thus, the small water clusters of only 2–3 water molecules in diameter may already be expected to exhibit the super-Arrhenius dynamics associated with the relaxing cage effect. Therefore, we believe that the essentially isotropic relaxation function that we used may adequately describe the dynamics of confined water in our experiment. We note that for a system with even narrower cylindrical pores, which can accommodate only single-molecule water chains, the use of the strictly one-dimensional diffusion model may be required.

The dynamic crossover from super-Arrhenius to Arrhenius behavior occurs at the same temperature as reported for 14 Å CMK and double-wall carbon nanotubes (CNT) with 16 Å diameter pores. While this crossover appears to be a common feature of water confined in various systems, its mechanism remains a hotly debated topic. One possibility is that the transition indicates some change in the cooperative dynamic properties of water that are represented by the super-Arrhenius alpha-relaxation. There have been suggestions that the crossover manifests either the disappearance of the alpha-relaxation, when only the beta-relaxation is left below the crossover temperature, or decoupling of the alpha- and beta-relaxation processes below the crossover temperature.

Our results show that the dynamic crossover temperature in water confined in the smallest carbon nanopores studied to date does not differ from that observed in water confined in larger hydrophobic nanopores. Even though in the very small carbon nanopores that we studied the water dynamics slow down greatly, the dynamic transition remains qualitatively unchanged. Figure 3 shows the average relaxation time of water molecules at the dynamic crossover temperature for various confining substrates as a function of pore size. Neither the hydrophilic silicate confinement, nor the hydrophobic carbon-based confinement shows a systematic trend in the $\langle \tau \rangle$ of water molecules at the crossover temperature. It is worth...
mentioning that CDC has a network of interconnected pores, just like zeolites, but no structural periodicity. Nevertheless, the dynamics of water confined in the smallest hydrophobic pores so far studied exhibit the longest relaxation times.

It should be mentioned that Doster et al. [30] claimed that there was no crossover in the dynamics of hydration water on a protein, even though the average relaxation time presented in that work deviated from the VFT dependence below 200 K. Interestingly, the reported relaxation time obtained for the protein hydration water at 200 K exceeded 100 ns [30], which is longer than the relaxation times at the crossover temperature reported in fig. 3 of the current work. This is despite the fact that water on the protein surface [30] is not nearly as spatially confined as the water in the ultra-tight pores studied in the current work. The relaxation times obtained for the protein hydration water at temperatures lower than 200 K were in the range of hundreds of nanoseconds [30], which seems to be far beyond the resolution attainable using a neutron backscattering spectrometer.

We have presented the results of quasielastic neutron scattering studies on dynamics of water confined in sub-nanometer carbon pores. The average relaxation time displays an apparent crossover in the temperature dependence at 190 K, from the high-temperature super-Arrhenius to low-temperature Arrhenius behavior. The average relaxation time of water molecules at the crossover temperature becomes much longer in smaller CDC pores. The crossover temperature observed in our study is similar to that reported for water confined in larger carbon pores. Thus, the dynamic crossover temperature in water in, perhaps, the smallest carbon nanopores that water can enter under ambient conditions does not differ from the crossover temperature in water confined in larger carbon nanopores.

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