Dynamic mechanical analysis of supercooled water in nanoporous confinement

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received 3 June 2016; accepted in final form 25 August 2016
published online 14 September 2016

PACS 64.70.P- – Glass transitions of specific systems
PACS 65.40.De – Thermal expansion; thermomechanical effects
PACS 81.05.Rm – Porous materials; granular materials

Abstract – Dynamical mechanical analysis (DMA)($f = 0.2–100$ Hz) is used to study the dynamics of confined water in mesoporous Gelsil (2.6 nm and 5 nm pores) and Vycor (10 nm) in the temperature range from $T = 80$ K to 300 K. Confining water into nanopores partly suppresses crystallization and allows us to perform measurements of supercooled water below 235 K, i.e., in water’s so-called “no man’s land”, in parts of the pores. Two distinct relaxation peaks are observed in tan$\delta$ around $T_1 \approx 145$ K ($P_1$) and $T_2 \approx 205$ K ($P_2$) for Gelsil 2.6 nm and Gelsil 5 nm at 0.2 Hz. Both peaks shift to higher $T$ with increasing pore size $d$ and change with $f$ in a systematic way, typical of an Arrhenius behaviour of the corresponding relaxation times. For $P_1$ we obtain an average activation energy of $E_a = 0.47$ eV, in good agreement with literature values, suggesting that $P_1$ corresponds to the glass transition of supercooled water. The observation of a pronounced softening of the Young’s modulus around 165 K (for Gelsil 2.6 nm at 0.2 Hz) supports the conjecture of a glass-to-liquid transition in the vicinity of $P_1$. In addition we find a clear-cut ($1/d$)-dependence of the calculated glass transition temperatures which extrapolates to $T_g(1/d = 0) = 136$ K, in agreement with the traditional value of water.

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Introduction. – Water is not only of fundamental importance for life, its behaviour is of great relevance for biology, geology, chemistry, physics and technology. Despite a long history of research many properties of water are still far from being understood [1,2]. Some of them, e.g., the location of its glass transition temperature $T_g$ and the existence of a liquid-liquid phase transition [3,4] have been controversially discussed in the literature [2,5–12].

Unfortunately it is impossible to follow the relaxation time of bulk water continuously down to $T_g$, since it crystallizes not later than $T_H = 235$ K which corresponds to the homogeneous nucleation temperature. At high temperatures, i.e. above 235 K water is a very fragile liquid (Vogel-Fulcher relaxation time dependence) [13], while on the other side of the so-called “no man’s land” (150–235 K) it was found to be a “superstrong” liquid with fragility index as low as $m \approx 14$ for confined water [14] as well as for bulk LDL [15]. Recently such a low fragility index was explained in terms of quantum effects at $T_g$ [16] which later were experimentally found to show up also in a large isotope effect on the glass transition of water [17]. The difference in “fragility” for water was used by Ito et al. to propose the existence of a fragile-to-strong (FST) transition in supercooled water near 228 K. During recent years, several authors have looked for an FST in confined water [14,18] and biomaterials [19]. However, its interpretation is subject of intense debate [19–21]. Some authors [22–24] relate the change in the dynamics to a transition from high density liquid (HDL) to low density liquid (LDL) around $T_{FS} \approx 225$ K. Others explain it in terms of spatial confinement $d$ [2] that would limit the size $\xi$ of dynamically correlated regions to $d$.

Confining water in mesoscopic environments is a way to suppress crystallization and even avoid it in pores smaller than about 2–3 nm in diameter [25]. Here we present results of extensive dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA) measurements of water confined in mesoporous silica, Vycor and Gelsil with pore diameters $d$ of 10 nm (V10), 5 nm (G5) and 2.6 nm (G2) and discuss our results in the light of previous studies.
The main specifications of the SiO$_2$ pores are randomly oriented with mean ratio of pore diameter over pore length $d/l \approx 0.23$. Cylindrical voids were sanded to gain parallel surface plains. Cleaning was done in a 30% H$_2$O$_2$ solution at 90°C for 24 h, followed by drying at 120°C in a high-vacuum chamber also for 24 h. Filling with distilled water was done by spontaneous imbibition [30].

For thermal expansion measurements we used a TMA 7 (Perkin Elmer). To study the slow dynamics of confined supercooled water, we performed Dynamic Mechanical Analysis (DMA) measurements (Diamond DMA and DMA 7, Perkin Elmer) as a function of frequency $f$ (0.01–100 Hz) and temperature $T$ (80–300 K).

The samples were mounted in a cell and rapidly cooled down. Two different cooling procedures, i.e., with a rate of about 1 K/min to 80 K as well as quenching the samples in liquid nitrogen have led to identical results in subsequent heating runs. The real $Y'$ and imaginary $Y''$ parts of the complex Young modulus $Y^* = Y' + iY''$ were measured in parallel-plate geometry. They are calculated from the elastic compliance tensor $S^*$, which is determined from the relation between the sample strain appearing in response to the applied dynamic force as well as the phase shift $\delta$ between dynamic force and sample strain. Details of the DMA method are given in refs. [31,32].

Most of the measurements were performed by heating from 80 K with a heating rate of 1.5 K/min. To avoid breaking of the sample we stopped every heating run around 230 K, cooled down the sample to 80 K and started the next heating run with another measurement frequency. In this way we measured $Y^*$ as a function of $T$ and $f$. We also measured thermal expansion of the samples during cooling and heating using a TMA7 (Perkin Elmer). The results are shown in fig. 1. The corresponding melting and freezing temperatures shown in the inset of the figure were calculated from the maxima of the derivatives of thermal expansion, i.e., of $\alpha = 1/L_0 \partial \Delta L/\partial T$.

One clearly observes a decrease of the freezing and melting temperatures with decreasing $d$ in agreement with previous observations [33] accompanied by a broadening of the transitions. From these data it is obvious that a considerable amount of water crystallizes even for the smallest pore size of 2.6 nm.

Although these data are helpful to get a first glance on the state of the system, to learn more about the corresponding structural dynamics we have to inspect the results of DMA measurements. Figure 2 shows a typical pattern of $Y'$ and $Y''$ for water in V10 as a function of $T$. We now determine the parameters of the supercooled water in nanoporous confinement. The observed pronounced downshift of $T_g$ with decreasing pore size—not so clearly seen by other methods—yields new insights into the glass freezing behaviour of supercooled water. Analysis of the data suggests that the pore size dependence of $T_g$ is an interfacial rather than a finite-size effect.

**Experimental results.** Table 1 summarizes the main specifications of the SiO$_2$-based nanoporous host-materials, obtained from N$_2$ adsorption and SAXS experiments [26–28]. Vycor originates from spinodal decomposition, resulting in a skeleton of nearly pure SiO$_2$ containing a network of interconnected nm-sized pores of narrow pore size distribution (PSD) [27].

| Properties                  | V10      | G5       | G2       |
|-----------------------------|----------|----------|----------|
| Pore size (nm)              | $10 \pm 0.5$ | $5 \pm 0.8$ | $2.6 \pm 1$ |
| Porosity $\Phi$             | 0.4      | 0.54     | 0.36     |
| Pore volume $V_{pore}$ (cm$^3$/g) | 0.224    | 0.7      | 0.4      |
| Pore surface area $\Omega$ (m$^2$/g) | 90      | 580     | 600      |
| $\Omega/V_{pore} \times 10^8$ (cm$^{-1}$) | 4.5      | 8.3      | 15       |

Table 1: Characteristic parameters [26–28] of porous silica samples.
measured with a DMA7 during heating and cooling with a rate of 1 K/min at 40 Hz. The abrupt increase of $Y'$ around 265 K which is accompanied by a peak in $Y''$ relates to the freezing of water in the pores. At lower $T$ a second peak ($P_1$) at about 165 K (1 Hz) in $Y''$ is observed which is accompanied by an “S-shaped” anomaly in $Y'$, resembling a typical relaxation behaviour.

It should be noted that the $T$- and $f$-dependencies of $Y'$ and $Y''$ throughout the paper reflect the anomalies of water in the pores, since the background of the unfilled silica samples behaves completely normal, i.e., $Y'$ varies less than 0.5% and tan $\delta < 0.01$ [28] over the whole measured $T$-range.

Figure 3 displays the $T$-dependence of $Y'$ and tan $\delta$ for G5 filled with water, measured at 3 Hz. In addition to the melting of water in the pores one observes a second process at 273 K which corresponds to the melting of surface water. Similar as for water in V10 a clear relaxation peak ($P_1$) around 165 K (3 Hz) is observed, which is accompanied by a distinct minimum in $Y'$ around 180 K (at 3 Hz), which also depends on $f$. In G2 filled with water the additional peak $P_2$ (fig. 4, bottom), which appears now at lower temperature (~200 K) as compared to G5, is rather pronounced. In addition the minimum in $Y'$ around 170 K (at 3 Hz) is now also strongly developed (fig. 4, top).

**Discussion.** – To analyse the data, especially the origin of the $P_1$-process, we determined time constants $\tau = 1/(2\pi \nu_m)$ from the loss peak frequencies $\nu_m$ and summarize the results in an Arrhenius diagram (fig. 5). The straight lines in fig. 5 indicate that the relaxation times corresponding to the $P_1$-process follow thermal activation according to $\tau = \tau_0 \exp(\Delta E/k_B T)$ with $d$-dependent activation energies. This results in a downshift of the peak $P_1$ with decreasing $d$ (fig. 6). The present activation energies (fig. 5) compare well with literature data [34–36]. Sjostrom et al. [36] performed calorimetry and dielectric measurements of water confined in MCM-41 with $d = 2.1$ nm (C10) and 3.6 nm (C18). They found that in C10 no ice formation occurs, whereas for C18 ice formation becomes substantial. However, not all water crystallizes in C18. Some
regions of capillary condensed water remain liquid even at low $T$. The authors attributed the dielectrically observed process with activation energy of $E_a \approx 0.47$ eV for C10 and C18 to the relaxation of amorphous water.

Cerveny et al. [11] performed broadband dielectric spectroscopy measurements of supercooled water confined in clay ($d = 1.5$ nm) and in white bread and compared it to various biological systems. They also obtained an average activation energy of $E_a = (0.46 \pm 0.04)$ eV and the temperature where $\tau = 100$ s was extrapolated to $T(100s) = (139 \pm 3)$ K. Traditionally this temperature was associated with the glass-to-liquid transition [2,9,14] of supercooled water.

Cerveny et al. [11] related the $P_1$ relaxation to a local process of the Johari-Goldstein [37] type. They located the glass transition at $T_g = 160–165$ K for bulk water and about 175 K for confined water (depending on the confining system). We do not think that the process $P_1$ which we detect in our DMA measurements is a local process.
The pronounced minimum in $Y'$ around 170 K at 0.2 Hz (fig. 4) in G2, which in G5 occurs at a higher $T$ of about 180 K, suggests that a considerable amount of water in the pores is in a liquid (probably ultraviscous) state which below this minimum in $Y'$ transforms to glass. Support for this scenario comes from recent neutron scattering data on amorphous solid water [8], which revealed the onset of long-range diffusive motion of water molecules above 121 K, marking the onset of a glass transition with its endpoint at $T_g = 136$ K. In our setup this transformation to glass is accompanied by an increase of Young's modulus. For a semi-quantitative analysis we adopt the so-called “pea-in-pod” model of ice formation in Vycor, proposed earlier by Sellevold and Radjy [38]. In their model they assume that inside the complex pore channels of Vycor (in their case $d = 4$ nm) the thicker regions contain crystalline ice, whereas in the thinner channels supercooled water can still exist. A sketch of this situation is given here in the inset of fig. 3. The volume fraction of crystal vs. liquid water can vary with pore size. I.e., in Vycor 4 nm about 55% of water was found to consist of ice [39,40]. With lowering temperature the water transforms to glass and cements the ice and the silica matrix effectively together, thereby increasing Young’s modulus (figs. 2–4).

As shown in fig. 6 the glass-to-liquid transition depends on the pore size. Extrapolating the relaxation times obtained for water in different confinements (fig. 5) to 100 s yields a perfect $(1/d)$-dependence of $T_g(d)$. A naive extrapolation to $1/d → 0$ intercepts at $T_g^{bulk} = 136$ K, in agreement with the traditional glass transition temperature of supercooled bulk water. However, since a considerable amount of water in the pores is crystalline [38–40], we have to take into account, that the effective average available volume of supercooled water is smaller than the nominal one, and thus we are dealing with an effective diameter $d_{eff}$. For a fair extrapolation to bulk $T_g$ we need to know the amount of supercooled water and its geometrical location for different $d$. Let us discuss several scenarios in the light of complementary literature data. Figure 7 shows a comparison of two quite different situations. In both figures we plotted the glass transition temperatures (purple full squares) determined from the measured peak shifts $T_g(d)$ extrapolated to 100 s. The purple line is a linear fit which extrapolates to $T_g^{bulk} = 136$ K. Now the problem appears how to estimate the effective size of supercooled water in the pores. We can use our thermal expansion data (fig. 1) to get an estimate of the volume ratios of ice in the different pores, although we cannot estimate its location. Using the different values for $\Delta L_0/L_0$ in fig. 1 we calculate the relative volume changes due to ice formation in the various pores. Together with the porosities of Gelsils and Vycor [41], we obtain $\Delta V/V_0 = 8\%$ for V10, 6.7% for G5 and 4% for G2. Since the volume change of bulk water at freezing is about 9%, a simple calculation yields for the relative volume $V_{sw}/V_{pore}$ of supercooled water in the different pores $\approx 11\%$ for V10, $\approx 30\%$ for G5 and $\approx 56\%$ for G2. To proceed we assume two quite different extremes of ice/water distributions: i) Making the assumption that $d_{eff} = (V_{sw}/V_{pore})^{1/3} \times d$, we obtain for the renormalized $d_{eff} \approx 5$ nm for V10, 3.3 nm for G5 and 2.1 nm for G2. An extrapolation (blue line in fig. 7) would then lead to a bulk $T_g$ that is not far from 136 K. This however implies that even for regions with a size of 5 nm water exists in its supercooled state, a situation that is hardly acceptable. ii) Another possibility would be to use a “core-shell” model of ice and supercooled water. Assuming spherical pores of Gelsil [33] and cylindrical pores for Vycor [27], $d_{eff} = d [1-(1-V_{sw}/V_{pore})^{1/3}]$ with $\gamma = 1/3$ or 1/2 for spherical or cylindrical pores, respectively. Interestingly enough, independently on the surface to pore volume fractions we obtain in all three cases $d_{eff} \approx 0.6$ nm, which corresponds to one layer of supercooled water. Although these estimations are rather rough, they suggest that there are not more than about two layers of supercooled water taking part in the glass freezing behaviour of Vycor and Gelsils. This is in good agreement with recent Ultrafast Optical Spectroscopy measurements of water in Vycor (4 nm) [40]. In this scenario the observed size dependence of $T_g$ cannot be explained as a finite-size effect, but should be rather understood as a surface effect, in the sense that different pore sizes $d$ imply different curvatures $\propto 1/d$. If we assume that $T_g$ depends on curvature, we can directly extrapolate (fig. 7) the observed $\Delta T_g(d) \propto 1/d$ to $T_g$ of bulk water with zero curvature.

Although the issue on the value of $T_g$ of bulk water has been controversially discussed and yet no final consensus seems to be reached [2], there are strong arguments in favour of the classical value of 136 K [21,42,43].
Finally, let us say a few words about the possible origin of the observed $P_2$-process (figs. 4, 5), which exhibits a similar activation energy ($E_a \approx 0.46 \text{eV}$) as $P_1$. It is tempting to relate the two peaks $P_1$ and $P_2$ to the two different principle radii $r_1$ and $r_2$ of curvature, which exist for a general surface. If for a cylindrical surface as in Vycor $r_1 \approx r_2$ and for Gelsil $r_1 \neq r_2$ the presence (absence) of $P_2$ in Gelsil (Vycor) could be easily understood.

Another possible explanation can be found by a comparison of the present data to previous DMA measurements of molecular glass-forming liquids, e.g. salol [41,44], toluene and o-terphenyl [45] in confinement. For salol confined in Vycor [46] and Gelsil [44] we obtained results which resemble the present behaviour of water in very detail especially in Gelsils. At low temperatures we found two relaxation peaks at $T_{g1} < T_{g2}$ in $Y''$ accompanied by a double “S-shaped” temperature dependence of $Y'$. In these systems, we could identify the two peaks unambiguously. The one at $T_{g1}$ was assigned to a glass transition of molecules in the core of the pores, whereas the other one at $T_{g2}$ originates from molecules close to the pore walls. Due to the strong attractive interaction of salol-molecules with the pore wall the dynamics of the interfacial molecules is considerably slowed down, resulting in an increased $T_g$. We think that a similar mechanism is also responsible for the $P_2$-relaxation process observed here for water in G2 and G5. Calculating the surface to volume ratios for the different pores (table 1), we obtain values $\Omega/V_{\text{pore}} = 4.5 \times 10^6 \text{cm}^{-1}$ for V10, 8.3 $\times 10^6 \text{cm}^{-1}$ for G5 and 15 $\times 10^6 \text{cm}^{-1}$ for G2, which support the assumption that $P_2$ is a surface effect and thus mostly pronounced in G2 filled with water. This is also corroborated by recent computer simulations [47] and experiments [48], where a strong slowing-down of the dynamics of water and glass-forming methanol molecules were found, when approaching hydrophilic pore walls. Note, however, that $P_2$ occurs close to the temperature anticipated for the liquid-liquid transition [2,3] between a high- and low-density liquid phase in bulk water. Thus, we can not exclude that $P_2$ is a signature of this transition occurring here for interfacial water. This interpretation would be in agreement with conclusions in a previous calorimetric and neutron scattering study on water in Vycor [49].

Summarizing, we have shown that the dynamic mechanical analysis technique provides novel additional information on the low-frequency dynamics of water in nanopores. A distinct pore size dependence of the glass transition temperature of confined supercooled water was for the first time detected from a macroscopic mechanical experiment. Analysis of present thermal expansion data for different pore sizes indicates that the supercooled water is most probably arranged in a shell of maximal two layers, independently of the size of the pores. Thus, the observed pore size dependence of $T_g$ cannot be a finite-size effect. The new physical picture that emerges then is that $T_g$ depends on the mean curvature $\kappa \propto 1/d$ of the corresponding pore surface, which for zero curvature ($\kappa \propto 1/d = 0$) extrapolates to $T_g(0) = 136 \text{K}$, the traditional value of bulk water. Recent investigations [50] on polymer nanotubes confined in aluminum oxide templates have unambiguously shown that the shift of $T_g$ with different pore size is an effect of geometric curvature, rather than a finite-size effect.

It is remarkable, that the glass freezing behaviour of such a small amount of one or two layers of water can be detected in a macroscopic mechanical experiment, and we are confident that the present results will stimulate further acoustic spectroscopy measurements to explore the structural dynamics of confined water in a broader frequency range.

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