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The glass transition and fragility of supercooled confined water

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Abstract

In this paper we discuss the glass transition and fragility of supercooled confined water. We have used vermiculite clay, a molecular sieve and purple membrane as host materials in order to obtain confinements that are severe enough to avoid crystallization of the water, even in the (for bulk water) experimentally inaccessible temperature range 150–235 K. The clay and membrane have a 2D structure with a water layer thickness of 6 and 9 Å, respectively, whereas the molecular sieve contains cylindrical pores with a diameter of 10 Å. We show that one dielectric relaxation process, observed in the deeply supercooled regime, is very similar for the three investigated systems, as well as for water confined in other types of host materials, suggesting that it is relevant, although not identical, also for bulk water. At the lowest temperatures this process follows an Arrhenius temperature dependence with a relaxation time of 100 s at a temperature of approximately 130 K. However, an interesting crossover to a non-Arrhenius behaviour seems to occur at $T > 185$ K. We discuss the possible origins of the observed dielectric relaxation process and its relation to the present controversy regarding the glass-transition temperature of hyperquenched water, as well as a proposed fragile to strong transition of supercooled water.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

It is well known that the behaviour of water in confined geometries and near solid surfaces is of central importance in biology, geology and technology. Water is, for instance, essential for the functioning of all biomolecules and therefore a requirement for life. In living materials almost all water molecules are closely associated with the biomolecules and are located in highly confined geometries [1]. As a consequence it is important to establish to what extent the geometrical confinements and the surface interactions influence the bulk properties of water. This is the main reason why there is currently great interest in studying the structure

and dynamics of water in biological or other kinds of model systems for confined water, such as vycor glasses [2–6], zeolites [7, 8], clays [9–13], etc. However, there is also another important reason to study water confined in various host materials, because it provides a means to avoid crystallization and elucidate the properties of supercooled water in the (for bulk water) experimentally inaccessible temperature range of approximately 150–235 K [14]. Thus, although confinements generally affect the structural and dynamical properties of water, it is nevertheless possible to make predictions about supercooled bulk water by studying supercooled water in severe enough confinements to prevent crystallization. The main purpose of this paper is to discuss the implications of results we have obtained from studies of supercooled water confined in vermiculite clay, a molecular sieve and purple membrane.

The relaxational dynamics of supercooled bulk water is currently a matter of intense research since it has recently been suggested that the glass transition T_g of bulk water is located somewhere in the temperature range 160–180 K [15, 16] (it should be noted that this idea is not really ‘recent’ since already in 1984 MacFarlane and Angell [17] suggested that $T_g < 160$ K for bulk water), which is a considerably higher temperature than the previously accepted value 136 K [18]. According to Angell the feature at 136 K in the differential scanning calorimetry (DSC) data of hyperquenched glassy water [18] is due to enthalpy relaxation rather than the real glass transition. This enthalpy relaxation is an annealing effect of hyperquenched glasses that gives rise to a so-called ‘shadow glass transition’ that should occur at a temperature about 20% below the real glass transition, which then never can be observed for glassy bulk water due to rapid crystallization (at 150 K) before T_g is reached [16]. Thus, if Angell’s interpretation is correct, this means that the T_g of bulk water can never be directly observed.

Another important issue, which also has been widely debated [13, 17, 19–21], concerns the ‘fragility’ of supercooled water. Using Angell’s fragility concept [22, 23], a supercooled liquid is termed fragile when its viscosity and related main (α -) relaxation time τ_α exhibit a highly non-Arrhenius temperature dependence, typical for ionic and van der Waals systems. In contrast, a supercooled liquid which shows a temperature dependence close to the Arrhenius law is denoted strong, reflecting that the material is held together by only strong (commonly covalent) bonds forming a network structure. It is well known that water above 235 K is one of the most fragile liquids that have ever been studied [19] and that the temperature dependence of its viscosity seems to follow a power law diverging at about 228 K [24–26]. However, since the consensus for the last two decades has been that T_g (i.e. the temperature for which $\tau_\alpha \approx 100$ s) is located at about 136 K (and still there are, at least, no indications that it should be above 180 K) this implies that the temperature dependence of τ_α must change from its power law dependence somewhere below 235 K. For this reason, it has been proposed that supercooled water undergoes a fragile to strong transition around 228 K, and that it is due to an end point in the formation of a hydrogen bonded tetrahedral network structure [19]. Such a crossover is, of course, a very unusual behaviour for a supercooled liquid, but it should be noted that similar fragile to strong transitions have appeared in simulations of BeF_2 and SiO_2 [27, 28], which also form tetrahedral network structures and furthermore exhibit many of the peculiarities (e.g. a density maximum in the liquid state) typical for bulk water [27–29].

In this paper we will discuss some new and previously published results from dielectric spectroscopy [13], neutron spin-echo (NSE) [30], and differential scanning calorimetry (DSC) measurements on fully hydrated vermiculite clay, a molecular sieve and purple membrane. The systems were chosen so the confinements are severe enough to prevent crystallization of water in the supercooled regime, while the surface interactions and pore geometries are different in the three systems. In the case of clay and purple membrane the interlayer water is located in (2D) slit pores, whereas in the molecular sieve the water molecules are located in (1D) cylindrical pores. The surface interactions are also distinctly different in the three systems

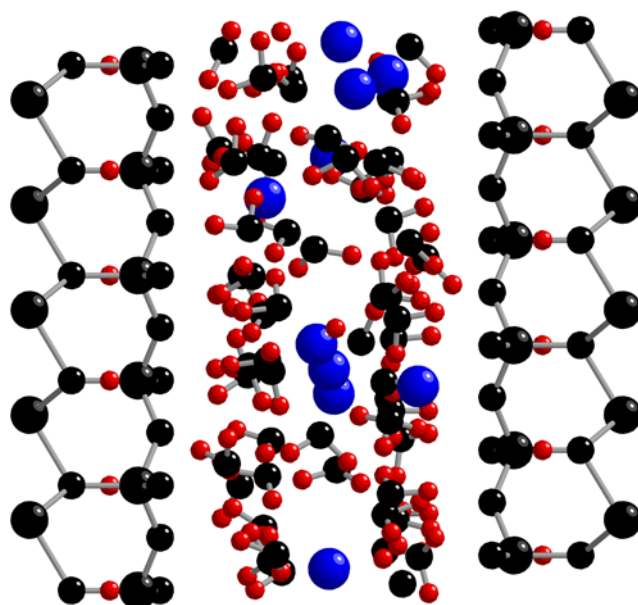


Figure 1. A plausible molecular snapshot of the clay platelets and the interlayer water and Na^+ ions (largest spheres) in the fully hydrated Na-vermiculite clay. This figure is reproduced with permission from ref [34].

(and additionally, the vermiculite clay contains interlayer Na^+ ions which have a strong tendency to form hydration shells), which implies that both the structure and translational diffusion of the confined water are expected to be widely different in these systems. However, we will show that the most pronounced relaxation process observed by dielectric spectroscopy is very similar for the investigated systems, as well as for water confined in other types of host materials [31], indicating that this process has basically the same origin in all systems. This means that it must be due to confined supercooled water, and furthermore that it is only weakly affected by the geometrical and chemical nature of the confinement. We will discuss whether this process corresponds to the α -relaxation of bulk water or if it is due to a more local secondary (β -) relaxation. The interpretation of this process will obviously also affect the T_g -value of water, which currently is a topic of major concern [15–17, 32, 33].

2. Water in clay

Let us first discuss some previously published results [13, 30] on a fully hydrated Na-vermiculite clay. In this system, the effective thickness of the confined water is 6.4 Å, corresponding to roughly two layers of water molecules (see figure 1). Thus, the motion of the water molecules is substantially restricted in the direction perpendicular to the clay platelets, but in the other two dimensions there is no restriction at all (except for the hydrated Na^+ ions). This is an advantage if we are interested in elucidating dynamical properties, which are of relevance also for bulk water, since it has been shown for confined glass formers in general that the effect on the dynamics is more marked the more dimensions are confined [35]. Also dielectric inhomogeneity effects are most pronounced in three-dimensional confinement [36]. The insensitivity of the main relaxation time to the present confinement has been verified for other glass formers that we have studied. It has been shown, see figure 2 for example, that

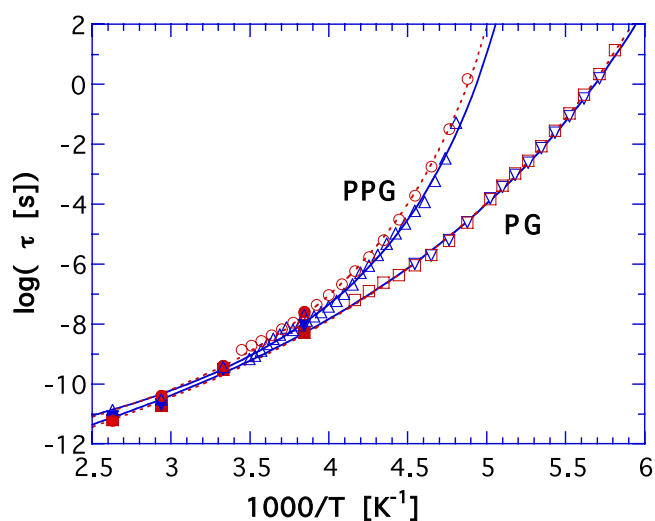


Figure 2. Temperature dependences of relaxation times for propylene glycol (PG) and poly(propylene glycol) (PPG), with a molecular weight of 4000, in bulk (squares and circles, respectively) and confined in Na-vermiculite clay (triangles). The dielectric α -relaxation times are given by open symbols whereas the average relaxation times from quasi-elastic neutron scattering are marked with filled symbols. Note the excellent agreement between the average relaxation times from neutron scattering and the dielectric α -relaxation times, evident from the simultaneous fitting with VFT functions (dashed curves for bulk and solid curves for confined liquids).

the relaxation times of both the α -process as well as the secondary β -process are basically unaffected compared to bulk for a wide range of molecular glass formers, such as propylene carbonate (PC), propylene glycol (PG) and its oligomers, and 3-fluoriline (3-FAN) [37, 38]. This may suggest that the relaxation times observed for water intercalated in the clay should also be similar to bulk, although we are now unable to make a comparison for temperatures below 235 K. However, this does not seem to be the case according to the average relaxation times $\langle \tau \rangle$ from NSE measurements [30] performed on the MUSES spectrometer at the Laboratoire Leon Brillouin (LLB), Saclay, France, shown in figure 3. The clay sample was fully hydrated with H₂O and the resulting relaxation times were obtained for an elastic momentum transfer (Q) vector of 1.0 Å⁻¹. The sample was oriented such that the elastic Q -vector was parallel to the clay platelets. Figure 3 shows clearly that $\langle \tau \rangle$ is larger than for bulk water in the temperature range 250–320 K and that the difference increases with decreasing temperature. The reason for this is that a major fraction of the water molecules are strongly bound to the interlayer Na⁺ ions, forming hydration shells with a considerably reduced translational diffusion constant. Thus, in general, the water dynamics in the clay is considerably slower than for bulk, but it should be noted that some of the water molecules in the clay are not interacting with the interlayer Na⁺ ions, and these molecules show more bulk-like dynamics [10]. The widely different local environments of the intercalated water molecules give rise to a substantially broader distribution of relaxation times compared to bulk water (the stretching parameter obtained from a Kohlrausch–Williams–Watts (KWW) [39, 40] fit to the data is as low as about 0.35 for $T < 280$ K [30]). The different behaviour of water compared to other molecular liquids intercalated in the clay [37, 38] is most likely due to the high density of hydrogen bonds in water and the strong tendency of the intercalated Na⁺ ions to hydrate, as mentioned above.

In figure 3 it is furthermore evident that the temperature dependence of $\langle \tau \rangle$ can be described by the Vogel–Fulcher–Tammann (VFT) [42–44] function $\tau = \tau_0 \exp\left(\frac{DT_0}{T-T_0}\right)$, where

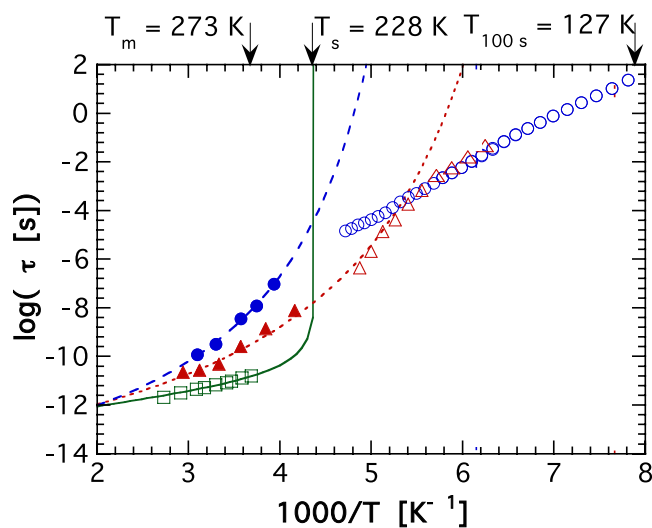


Figure 3. Relaxation times obtained for fully hydrated Na-vermiculite clay (circles) and molecular sieves with a pore diameter of 10 Å (triangles). Solid symbols correspond to average relaxation times obtained from NSE and empty symbols represent dielectric relaxation times. Relaxation times for the dielectric main process of bulk water [41] (open squares) are shown for comparison. The temperature dependences of the NSE times have been described by VFT functions (dotted and dashed curves for molecular sieves and clay, respectively), whereas the solid curve represents the proposed [22–26] power law behaviour of bulk water.

$\tau_0 \approx 10^{-14}$ s, $D \approx 9$ and $T_0 \approx 163$ K in our case. In the VFT function τ_0 represents the relaxation time at an infinitely high temperature, T_0 is the temperature where τ goes to infinity, and D is a parameter which determines the departure from Arrhenius behaviour, i.e. it distinguishes between strong and fragile supercooled liquids (high and low D , respectively). The low D -value indicates that our confined water behaves as a fragile supercooled liquid, although slightly less fragile than bulk water, in the temperature range >250 K. However, in this context one should note that NSE probes all water dynamics on the experimental timescale, and not only the motions related to the dielectric α -relaxation.

Figure 3 also shows the temperature dependence of the relaxation time corresponding to the most intense dielectric loss peak of water confined in the clay. These measurements were carried out on the broadband (10^{-3} – 10^9 Hz) high-resolution dielectric spectrometer, Novocontrol Alpha. Since the relaxation process shown in figure 3, which is not due to ice or the clay platelets, is the slowest and strongest clearly observable process and furthermore has a relaxation time of 100 s at approximately 130 K, i.e. close to the T_g -value [18] which was widely accepted for bulk water at the time of our study, it was interpreted as the α -relaxation of the confined water [13]. Provided that the interpretation is correct, the Arrhenius temperature dependence (see figure 3) of its relaxation time at low temperatures ($T < 215$ K) indicates that the intercalated water behaves like a strong supercooled liquid, in accordance with the proposed strong nature of supercooled bulk water at low temperatures [19]. However, in conflict with this interpretation is the symmetric shape of the peak [13]. This is not the common shape for an α -process, but rather the generally observed behaviour for a more local secondary process, termed β -relaxation. Moreover, the observed Arrhenius temperature dependence of its relaxation time is fully consistent with a normal β -process and, in fact, is very rarely seen for the α -relaxation in glass formers. With the new evidence that T_g of bulk water is located above 160 K [15–17] it is also less likely that our confined water should exhibit a glass transition

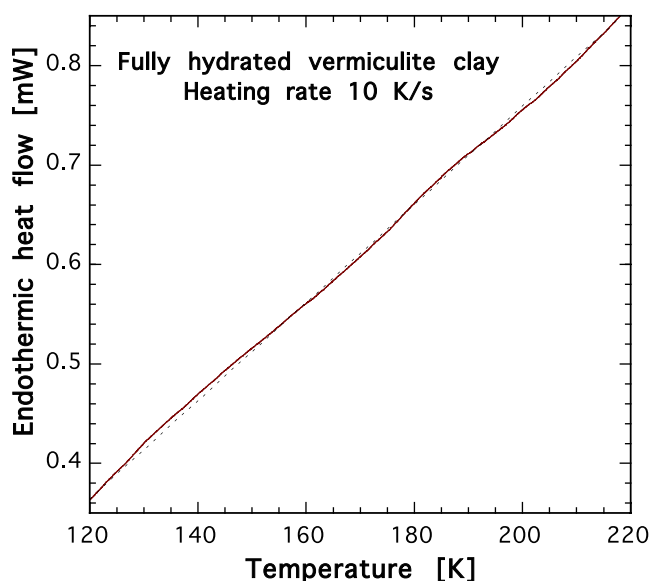


Figure 4. DSC measurement of endothermic heat flow during reheating (10 K min^{-1}) of a fully hydrated vermiculite clay. The dashed curve is just a guide for the eye to more easily observe the small deviations from a linear temperature dependence.

at about 130 K, considering that the high temperature diffusive dynamics of the intercalated water is slower than in bulk water, as discussed above (see figure 3 and [30]). This suggests that the observed loss peak, previously thought to be the α -relaxation, actually corresponds to a local β -relaxation. Nothing in the behaviour of the peak itself is inconsistent with this interpretation, but it is a problem that no other dielectric loss peak can be clearly observed on the low frequency side of the peak. Thus, if this dielectric loss peak is due to a β -relaxation why then is no α -relaxation present, as in the case of all the other liquids studied in the same confinement [37, 38]?

A similar problem is that we are unable to observe any clear glass transition in DSC measurements of water confined in the same fully hydrated vermiculite clay (as well as in the molecular sieve and purple membrane, as discussed below). Figure 4 shows that no clear glass-transition-like feature can be observed at 130 K, or any other temperature, for the intercalated water. One may argue that the confinement is too severe for observing both a dielectric α -relaxation as well as a calorimetric glass transition, but since both the α -relaxation and the glass transition have easily been observed for all the other liquids we have studied in the same confinement (with an even smaller layer thickness) [45, 46] this appears to be an unlikely explanation, particularly since it has been equally difficult to observe the glass transition for water in other confinements. In an attempt to understand this difficulty and to clarify the nature of the strong loss peak we have recently investigated the relaxation behaviour of water confined in other host materials. Here, we will discuss some new results on the molecular sieve and purple membrane.

3. Water in a molecular sieve

The molecular sieve we used was purchased from Sigma-Aldrich and is denoted M-3135. Its chemical composition is approximately $\text{Na}_2\text{O}-3\text{SiO}_2-\text{Al}_2\text{O}_3$, and it contains well-defined

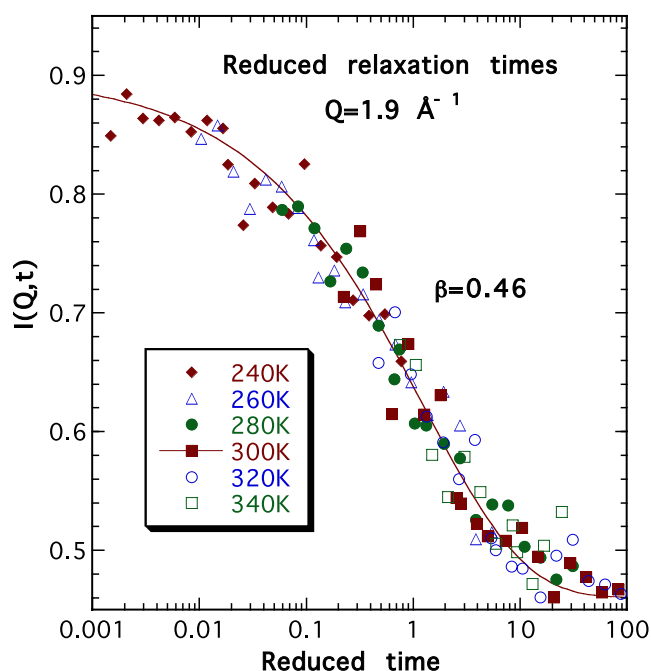


Figure 5. Intermediate scattering functions $I(Q, t)$ on a reduced timescale for a fully hydrated molecular sieve. The data points for each temperature have been time rescaled so the typical relaxation time τ_{KWW} that was obtained for each temperature (by a KWW fit to the data) was normalized to unity. The figure shows that the NSE data can be described by a KWW function with a stretching parameter $\beta_{\text{KWW}} = 0.46$ for all temperatures.

cylindrical pores with a diameter of 10 Å. The surfaces of these pores are polar and strongly hydrophilic. The molecular sieve was dried in a vacuum oven and thereafter rehydrated in a 100% relative humidity of H₂O in the case of the dielectric measurements and in D₂O before the NSE experiments. In this way the samples contained approximately 18 wt% water.

The NSE and dielectric relaxation times for the fully hydrated molecular sieve are also shown in figure 3. The average relaxation times $\langle \tau \rangle$ from the NSE measurements [47] (also performed on MUSES at LLB) were obtained in the temperature range 240–340 K for $Q = 1.9 \text{ \AA}^{-1}$, in order to maximize the coherent scattering contribution from D₂O. It was possible to fit the measured intermediate scattering function $I(Q, t)$ with a KWW function using a stretching parameter $\beta_{\text{KWW}} = 0.46$ for all temperatures. This is evident in figure 5, which shows reduced relaxation times for all the measured temperatures, i.e. the data were normalized so the typical relaxation time $\tau_{\text{KWW}} = 1$ for each temperature. In figure 3 it can be seen that $\langle \tau \rangle$ is less than one order of magnitude slower than for bulk water at the highest temperatures (320 and 340 K), but this difference increases with decreasing temperature. As for the NSE data on the fully hydrated clay the data points are reasonably described by a VFT function where, in this case, $\tau_0 \approx 3 \times 10^{-14} \text{ s}$, $D \approx 10$ and $T_0 \approx 130 \text{ K}$. Thus, the fragility of the water in the molecular sieve (for $T \geq 240 \text{ K}$) is almost as high as for the water in clay, although the lack of ions in the pores of the molecular sieve gives a faster average relaxation rate in this case. It should further be noted that the NSE data on the molecular sieve was obtained at a higher Q -value (1.9 \AA^{-1}) compared to the clay (1.0 \AA^{-1}), and this also contributes to the faster dynamics of water in the molecular sieve.

The dielectric data of the molecular sieve exhibits two clear relaxation processes: a slow process, which at low temperatures (<220 K) shows an Arrhenius temperature dependence with a very high activation energy of 1.0 eV, and a faster process which at low temperatures (<185 K) is almost identical to the main relaxation in the fully hydrated vermiculite clay (see figure 3 and [48]). The slow process (not shown in figure 3) is most likely due to the motion of water molecules that are strongly interacting with the walls of the very hydrophilic pores, whereas the faster process is probably due to the motion of water molecules which are mainly interacting with other water molecules, since it is so similar to the main process in clay at low temperatures. The fast process does not only show the same relaxation time and activation energy (0.42 eV) at a given (low) temperature, its dielectric loss peak is furthermore described by a similar symmetric Cole–Cole function. This almost identical behaviour at low temperatures for water confined in clay and a molecular sieve is interesting to note, but even more notable is the strong deviation from the low temperature Arrhenius behaviour at about 185 K. For $T > 185$ K the temperature dependence of the dielectric process can be described by approximately the same VFT function as was used to fit the NSE data; see figure 3. Thus, it appears that this process exhibits a transition from Arrhenius behaviour at low temperatures to a VFT behaviour at higher temperatures. Possible explanations for this dynamical ‘crossover’ will be given in the discussion section below.

4. Water in purple membrane

Purple membranes, extracted from *Halobacterium salinarum* [49], consist of a layer structure similar to clays, with the exception that each membrane layer is much thicker (about 49 Å, compared to the 9 Å in the case of clay) and contains various lipid species as well as the membrane protein *bacteriorhodopsin* [50]. An advantage of this system as a model system for studies of supercooled water is that the interlayer spacing of water does not contain any ions, in contrast to the clays, and a water layer with a thickness of about 9 Å can remain non-crystalline for temperatures up to 200 K, provided that the hydrated membrane is quenched directly into liquid nitrogen [51].

Recent dielectric measurements on such a fully hydrated purple membrane have shown [52] that the main process at low temperatures is also in this case almost identical to the process shown in figure 3 for the fully hydrated clay and the molecular sieve. Its temperature dependence follows an Arrhenius law at low temperatures, and, as in the case of the molecular sieve, a weak ‘crossover’ is observed at a temperature around 190 K [52]. The dielectric data of purple membrane will not be further discussed in this paper, but it is important to note that the observed main relaxation process seems to be a very common dielectric feature of confined water at low temperatures since it has not only been observed in clay and the molecular sieve, but also in a wide range of other hydrated host materials [31]. Thus, all these systems exhibit a dielectric process with a relaxation time of 100 s at a temperature of approximately 130 K.

5. Discussion

In figure 3 the average relaxation times from NSE extrapolate to 100 s at the temperatures 200 and 166 K for water in clay and the molecular sieve, respectively. Considering that the average translation dynamics in clay is considerably slowed down by the interlayer Na^+ ions, both temperatures are realistic T_g -values, provided that T_g for bulk water is located in the temperature range 160–180 K, as recently has been suggested [15–17]. Thus, if the α -relaxation time of the confined water follows these extrapolated average relaxation times from neutron

scattering, as clearly was the case for PG and PPG shown in figure 2, then the α -relaxation is evidently invisible or very weak in the dielectric data, and the observed dielectric main process must correspond to a β -relaxation of the confined water. The clear deviation from an Arrhenius temperature dependence at about 185–190 K for water in the molecular sieve and purple membrane is then most likely caused by the merging of the observed β -process with an extremely weak or even invisible α -relaxation. (The reason that a similar merging effect is not observed for the water in clay would then be that the merging occurs at a higher temperature in this system due to the α -relaxation being slower, as indicated in figure 3.) Thus, the deviation from an Arrhenius behaviour of the β -relaxation can be seen as an indirect evidence for a merging with a non-observable α -relaxation. In figure 3 it is evident that such an interpretation is consistent with the NSE and dielectric data of the molecular sieve, since the assumed α -relaxation from NSE coincides with the dielectric β -relaxation in the merging region. What is further consistent with this interpretation is the symmetric shape of the dielectric loss peak, which is the common shape for β -processes, in contrast to α -relaxations. The question is, however, why we are unable to observe any dielectric α -relaxation? The answer might be that the severe confinement suppresses the amplitude of the α -relaxation (or even makes it disappear), relative to the amplitude of the β -process, even more than previously has been observed for PC, 3-FAN, PG and PPG intercalated in the same clay [37, 45]. A vanishing α -relaxation at low temperatures, even for comparably low degrees of confinements, as in the 9 Å thick water layer of quenched purple membrane, can further explain why no clear calorimetric glass transition is observed for the here studied samples. The finding that no clear calorimetric glass transition can be observed (and neither any dielectric α -relaxation if this scenario is correct) is an anomalous behaviour even for the present confinements, since it is easily observed for other liquids in similar confinements, or even in the same clay [45, 46] as mentioned above. This suggests that water behaves very differently, compared to most other liquids, in the deeply supercooled regime and that the rapid crystallization of supercooled bulk water in the so-called ‘no man’s land’ between 150 and 235 K [14] is not the only problem one has to face in dielectric and calorimetric studies of deeply supercooled water. It seems clear that a severe confinement prevents the calorimetric glass transition (and the dielectric α -relaxation if this scenario is correct) from existing, in contrast to what we have found for other liquids in the same confinements. Hence, the present approach to use geometrical confinements to avoid crystallization in the supercooled regime, and in that way be able to explore the glass transition and its related relaxational dynamics of the corresponding bulk liquids, had been a successful approach for all the other confined liquids we have studied, even if they had crystallized as easy as water. A possible explanation for the anomalous behaviour of supercooled water might be its strong tendency to form a hydrogen bonded 3D network, which may need to be completed and rather extended in all directions for the calorimetric glass transition and the dielectric α -relaxation to be present.

If the scenario given above is correct it seems that at least the confined water investigated here should exhibit an α -relaxation (if observable) following a VFT temperature dependence over the entire supercooled regime. Thus, in this case there is no evidence that deeply supercooled confined water should be a particularly strong liquid, and therefore no fragile to strong transition needs to be introduced, as has been proposed to occur for bulk water at a temperature around 228 K [19]. However, if instead the other possible scenario is correct and the observed dielectric main process represents the α -relaxation of the confined water, then it is obvious from figure 3 that the deeply supercooled water is a very strong liquid, with a fragility comparable to SiO_2 . The deviation from an Arrhenius temperature dependence at 185–190 K for molecular sieves and purple membrane can in this case not be explained by a merging phenomenon, but must be due to a fragile to strong transition of the confined water,

in accordance to what has been proposed for bulk water [19]. The data presented in figure 3 are also consistent with this interpretation, at least if one accept the symmetric shape of the dielectric loss peak, which in this case is interpreted as the α -relaxation, although this implies that the T_g of water must be located around 130 K, rather than in the recently suggested range 160–180 K [15–17]. Thus, if this scenario is correct it supports both the original interpretation of DSC data on hyperquenched water, giving a T_g at 136 K [18], as well as the more recently suggested fragile to strong transition in the supercooled regime [19]. However, one should note that the former interpretation of the dielectric data is probably more likely, particularly after the recent support from dielectric studies of supercooled water in other confinements [31, 53].

6. Conclusion

In this paper we have discussed different possible interpretations of dielectric data on water confined in vermiculite clay, a molecular sieve and purple membrane. Two possible scenarios are consistent with the experimental data. If the present results on confined water are reasonably relevant for bulk water, then these two scenarios give the following implications for supercooled water. The first scenario suggests that supercooled water behaves as a fragile liquid over the whole temperature range, and exhibits a glass transition in the range 160–180 K, as recently has been suggested [15–17]. The major problem with this interpretation may be the absence of a clearly observable dielectric α -relaxation of the confined water, although this finding is in agreement with an equally weak (or absent) calorimetric glass transition. The second scenario is consistent with a fragile to strong transition in the supercooled regime, as recently has been suggested [19], and a T_g -value close to the previously widely accepted value 136 K [18]. In this case the problems with the present data are the unusual symmetric shape of the dielectric loss peak corresponding to the α -process, and its unexpected insensitivity to widely different types of confinements.

Irrespective of which scenario gives the most appropriate description of the dynamics of supercooled water, it seems clear that its behaviour is anomalous compared to most other supercooled liquids, in one or another way. The present confinements seem to have an extraordinary effect on the dynamical properties of supercooled water, which gives rise to more experimental difficulties in the investigations of the ‘no man’s land’ than the rapid crystallization of bulk water.

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