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Dielectric Spectroscopy of Water Confined Between Aerosil Nanoparticles and in Vycor Nanoporous Glass

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The dynamic properties of water dispersed in compacted aerosils and confined in Vycor porous glass have been investigated by means of dielectric relaxation spectroscopy. The measurements were performed in the frequency range from 10^{-2} to 10^{7} Hz and in the temperature range from 123 to 300 K. Multiple relaxation processes in bulk water, in water dispersed with aerosil particles, and in Vycor glass were observed. By comparing the presence and absence of the processes in the different samples, it was established that part of the water in confinement crystallizes to a bulk-like ice, whereas the water close to the surfaces evolved to a different phase.

KEY WORDS: aerosils; confinement; dielectric spectroscopy; ice; surface relaxation; Vycor porous glass; water.

1. INTRODUCTION

Water is ubiquitous, and life depends on it. The substance covers two-thirds of our planet, whereas 70% of our body weight consists of it. Its importance can be further envisaged by the search for the compound, as the primary target, in recent missions to Mars. Although by now, through centuries of investigation, scientists know a lot about water, many questions still remain about this essential and, in many ways, mysterious substance [1–3].

Water can exist in at least 13 different forms of crystalline structures, most of them occurring at high pressures. Among these, nine are stable over some range of temperature and pressure and the other forms are

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metastable. The known stable forms of water at sufficiently low temperatures are in the crystalline state. Supercooled states of water are also known to exist. At ambient pressure the stable phase of ice is called ice I. There are two closely related forms of ice I: hexagonal ice Ih, which has hexagonal symmetry, and cubic ice Ic, which has a crystal structure similar to diamond. Ice Ih is the normal form of ice; ice Ic is usually formed by depositing vapor at very low temperatures (below 140 K). Amorphous ice can also be made by depositing water vapor onto a substrate at still lower temperatures [4]. If liquid water is cooled fast enough, freezing can be avoided altogether, and water then becomes a non-crystalline solid, known as glass. Water has a long list of anomalies and most of the peculiarities are observed at low temperatures. This makes the study of supercooled water interesting from a fundamental point of view. In this paper we attempt to supercool water by reducing its available volume by confinement and possibly to provide us with glassy water.

An easy way to supercool water is to destroy the hydrogen bonds between the water molecules [5]. This has been accomplished in several experiments by adding salt. Such experiments have led to changes in the glass transition temperature T_g, a boon for glass physics. However, this procedure leads to a drastic increase in the conductivity, thus causing problems for dielectric measurements. Another method adopted to supercool water has been to confine water in host materials such as vermiculite clay [6,7]. However, in all these reports the values of T_g are those of surface water. The group of Angell [3] has doubts about T_g of bulk water. A very recent paper [6] discusses the possibility that the generally accepted T_g of water may indeed be that of surface water. Results obtained from diverse materials—ranging from biological systems, mineral and synthetic systems, hydrogels, and vermiculite clay—compared in the paper show that $T_g = 136\,\mathrm{K}$ is indeed coming from surface or bound water. It seems that close to the surfaces, the hydrogen bonded network of water is distorted or replaced by surface interactions. This causes an affected cooperative α-relaxation, being indicative for the dynamic glass transition. Also, a local β-like process of water molecules interacting with the host material may have been observed in this diverse set of materials.

It has been seen in Refs. [5–7] that water can be supercooled in surface layers of vermiculite clay, because of the presence of intercalated sodium ions. It was found in these studies that for the case of a single layered water phase, all the hydrogen atoms are bound directly to the adjacent platelets, thus breaking the hydrogen bonds between the water molecules. Hydrogen bonds between the water molecules occurred in the two-water-layer phase, where it was additionally found that only half of the water molecules form a hydrogen bond to one of the clay surfaces.

Differential scanning calorimetry showed that approximately 24% of the interlayer water in the two-water-layer system crystallized at 235 K whereas the remaining water remained in the supercooled liquid state [7]. We expect similar behavior for water with hydrophilic aerosil nanoparticles (with a diameter of 7 nm), where the surface water may form hydrogen bonds with the hydroxyl groups on the particle surfaces. We also found in a dielectric study that liquid crystal molecules in the immediate vicinity of the aerosils behave differently from the rest of the molecules [8]. Thus, for a very low content of water in aerosils, where most of the water molecules are in the vicinity of the aerosil particles, we might expect to observe a supercooled state of water. We also investigate water in Vycor porous glass, where also water molecules are situated close to the surface of the pores (size around 7 nm) and different surface interactions might be present.

2. EXPERIMENT

We have studied water dispersed with hydrophilic aerosils and water confined in the random porous network of Vycor glass. Water was obtained from a Millipore ultrapure water system that provides water with a resistivity (a measure for the purity) larger than 18.2 MΩ·cm.

Aerosils were provided by Degussa Corp. We used hydrophilic aerosils of type A300. These aerosils are silica spheres with a diameter of 7 nm and a surface area of $300 \pm 30\,\mathrm{m}^2\cdot\mathrm{g}^{-1}$. On the surface there is one silanol (Si–OH) group per 0.28–0.33 nm^2. These –OH groups are available for hydrogen bonding, resulting in the hydrophilic character [9]. Before mixing with water, the aerosils were vacuum dried at 200°C for about 15 h. We prepared four samples, one with low aerosil concentration and three with high concentration. The low concentration sample contained 333% water by mass (thus 3.33 g water for each 1 g of aerosils); this sample was visually indistinguishable from bulk water at room temperature. For the other samples we first compressed the aerosils in a pellet of 20 mm diameter and 1–2 mm thick. Water was added by placing the pellet in a wet atmosphere. In this way, concentrations of 74, 29, and 13.4% of water by mass were added to the aerosils.

Vycor porous glass of Type 7930 was obtained from Corning Inc. From the manufacturer and Ref. [10], we know that there is a three-dimensional network of randomly interconnected pores. The mean pore size is 7 nm with a distribution width of 0.5 nm and the typical chord length is 30 nm. The glass was cleaned with hot nitric acid and washed with deionized water. Then it was baked overnight at 450°C and finally impregnated with water until saturated.

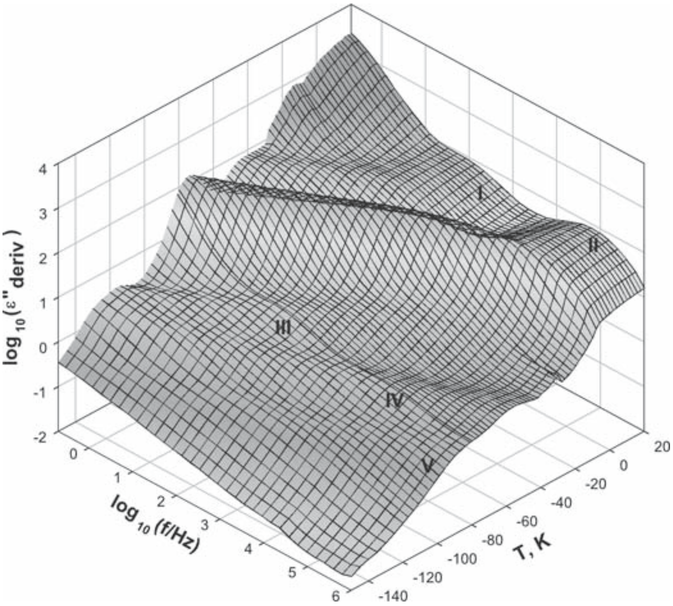

Fig. 1. Three-dimensional representation of the $\varepsilon''_{\mathrm{deriv}}$ spectrum of water confined to Vycor porous glass.

The complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ has been measured in isothermal frequency scans using a Novocontrol Alpha analyzer with an active sample cell. The frequency range was 10^{-2}–10^{7} Hz; temperatures ranged from 123 to 298 K. The temperature was controlled by a Novocontrol Quatro controller to 0.02 K stability. The sample cell was sealed with O-rings to prevent evaporation or absorption.

The data analysis was performed by interpreting the data using the Havriliak-Negami function [11]:

$$\varepsilon^*_{\mathrm{HN}} = \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j}{\left[1 + \left(i2\pi f \tau_j\right)^{1-\alpha_j}\right]^{\beta_j}} - i\frac{\sigma}{2\pi\varepsilon_0 f^n},$$

where ε_∞ is the high-frequency limit of the permittivity, $\Delta\varepsilon_j$ is the dielectric strength, τ_j is the mean relaxation time, and j is the number of the relaxation process. The exponents α_j and β_j describe the symmetric and asymmetric distributions of relaxation times. The term $i\sigma/2\pi\varepsilon_0 f^n$ accounts for the contribution of conductivity σ with n as a fitting parameter. This analysis is performed in two different ways. On the one hand, we fitted the original ε'' data to $Im\left(\varepsilon^*_{\mathrm{HN}}\right)$ with the WinFIT program from

Novocontrol. On the other hand, we fitted

$$\varepsilon''_{\text{deriv}} = -\frac{\pi}{2}\frac{\partial \varepsilon'}{\partial \ln f}$$

to

$$-\frac{\pi}{2}\frac{\partial Re\left(\varepsilon^{*}_{\text{HN}}\right)}{\partial \ln f},$$

a technique described in detail in Ref. [12]. This method eliminates the contribution of Ohmic conductivity to the spectrum and improves the separation of Debye peaks that are close to each other.

To verify to what extent both methods compare, we analyzed the data of water confined to the pores of Vycor glass using a direct fit to ε'' as well as a fit to $\varepsilon''_{\text{deriv}}$. Analysis of $\varepsilon''_{\text{deriv}}$ reveals five processes (Fig. 2). Analysis of ε'' reveals only the four slower processes, but these results are fully compatible with the $\varepsilon''_{\text{deriv}}$ ones: the relaxation times coincide where they are available from both methods. ε'' does not resolve the fastest one because it is very weak. This means that the results of both methods can be used interchangeably. Thus, it appears that for very weak processes the derivative approach is somewhat more sensitive. Although here the results for $\varepsilon''_{\text{deriv}}$ are better than those for ε'', it is sometimes desirable to use ε'': if ε' is scattered, taking the derivative increases the scatter. In the following, results from the method yielding the best result will be presented.

Both experimental and fitting errors are small, even with a large number of parameters involved. The typical relative experimental error in dielectric measurements with up to date equipment is usually considered negligible; the absolute error is not relevant for a discussion of the relaxation times. The quality of the fitting is verified quantitatively by reducing the deviation between fit and data below a certain (low) level. From Fig. 1, one can see that the processes are well separated. Thus, the different terms in the Havriliak-Negami expression do not influence each other strongly. Standard error estimates show that the error in the relaxation times is less than 1%.

3. RESULTS

3.1. Dielectric Relaxation of Water in Vycor Porous Glass

As can be seen from Fig. 1, the spectrum of water confined to Vycor porous glass, presented as $\varepsilon''_{\text{deriv}}$, shows a rich behavior. From the three-dimensional representation, we can distinguish five processes.

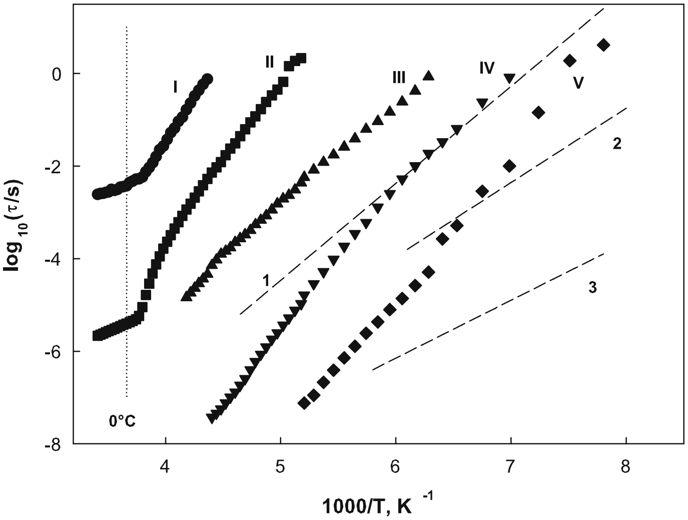

Fig. 2. Temperature dependence of the relaxation times for the relaxation processes observed for water in Vycor porous glass. For comparison, the relaxation processes observed for two-layered water in vermiculite clay [5] have been shown as dashed lines.

At high temperatures, the spectrum is dominated by two strong processes (I and II in Fig. 2); their dielectric strengths are more than ten times larger than those of the three other processes, and are quite constant. This suggests that process I and maybe also II are related to conduction phenomena, I probably being a Maxwell-Wagner type process. The nature of process III at this moment is unclear. It appears to branch from II, but it is much weaker and its activation energy suggests that it is more closely related to the faster processes IV and V.

The two strong processes I and II have a kink in their relaxation time behavior slightly below the melting point of bulk water. If we assume these processes to be related to conduction, then this might indicate that after a short supercooling due to confinement, (partial) freezing starts and the conductivity of the sample then changes. As this change is continuous and no other clear changes can be seen at other temperatures, this suggests that to a certain extent, the local structure of water in Vycor is already present before freezing starts. We regret the absence of high frequency data that could reveal from which temperature on the faster processes show up. This information can confirm or refute this last statement.

Processes IV and V have relaxation times comparable to processes 1 and 2 in the "2-H_2O vermiculite clay" from Ref. [5]. We will return in the discussion section to the interpretation of these processes.

3.2. Dielectric Relaxation of Aerosils with Low Water Content

In Fig. 3 we have summarized the relaxation times of our three aerosil samples with low water concentration. We will use the numbering introduced in Fig. 2 to identify the processes: processes with similar features will receive the same number. It should be remarked that the 13% and 74% samples have been fitted using ε'', whereas for the 29% sample, $\varepsilon''_{\mathrm{deriv}}$ was used.

The situation is most clear in the 13 and 29% samples, where the two faster processes nearly perfectly coincide with IV and V of Vycor. For the case of 13% water, the slow process is to be identified with II. The slow process in the case of 29% cannot be fitted very well, as it is at the edge of the range. It seems closest to III, but we will not consider it further.

Fitting of the 74% water sample was substantially more difficult. At lower temperatures, the identification with III–V seems reasonable. The deviations at higher temperatures can be explained by taking into account the much larger strength of III in this sample and the reduced visibility of relaxation processes due to the dominance of the conductivity. It even appears that the steeper high-temperature part of process III here can eventually be identified with process II from Vycor. The presence of such a process at lower temperatures can influence the fitting of the other processes. It was not possible to improve upon this result, so we cannot be entirely sure of the identification of the processes at high temperatures.

3.3. Dielectric Relaxation of Bulk Water/Ice and Aerosils with High Water Concentration

Both the data sets for ice and 333% water in aerosils have been analyzed using ε''. In both samples we see three, at first sight comparable, processes (Fig. 4). This suggests that the amount of aerosils added to the second sample is too small to induce important changes in the dynamics.

The fastest process in bulk ice cannot be related to any of the five seen previously and thus receives the number VI. It appears to be related to process 3 of Ref [5]. The fastest process in the aerosil sample matches process V in Vycor.

The middle process coincides with III in both cases. The slowest process falls in both cases in between I and II of Vycor. We will assign it II here, since we suggested a Maxwell-Wagner type process for I. A

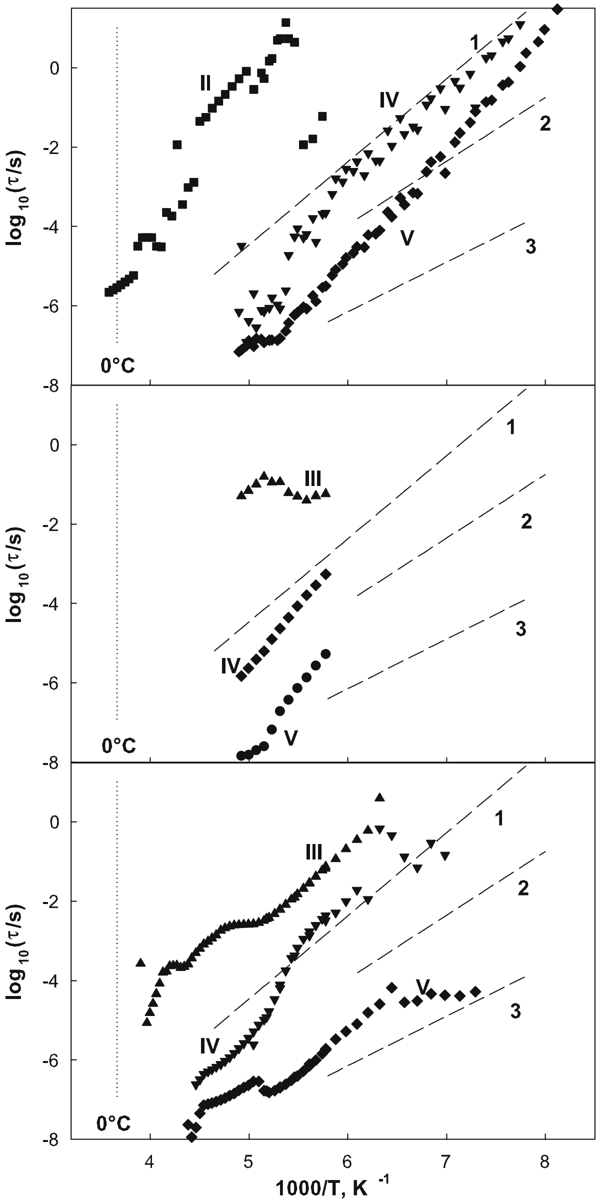

Fig. 3. Temperature dependence of the relaxation times for the relaxation processes observed for aerosils with (top to bottom) 13.4, 29, and 74% water. For comparison the relaxation processes observed for two-layered water in vermiculite clay [5] have been shown as dashed lines.

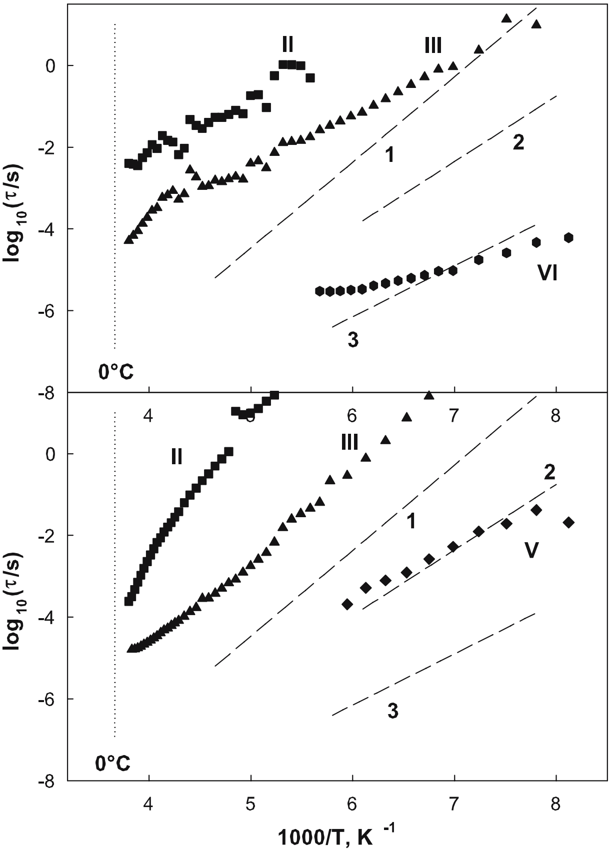

Fig. 4. Temperature dependence of the relaxation times for the relaxation processes observed for (top) bulk ice and (bottom) aerosils with 333% water. For comparison, the relaxation processes observed for two-layered water in vermiculite clay [5] have been shown as dashed lines.

Maxwell-Wagner type process would require the presence of regions with different dielectric permittivity ε and electrical conductivity σ [13]. It would be difficult to find a good motivation for the existence of such regions in a sample as bulk ice, although of course polycrystallinity can play a role.

An extra argument to associate this process with II is the fact that the high-temperature part of III in this sample actually coincides with II in Vycor, confirming that a process comparable to process II in Vycor is present here. The fact that the processes are here flowing over into each

Table I. Summary of the Occurrence of Relaxation Processes in the Different Water Samples

Vycor	74%	29%	13.4%	Ice	333%
I					
II	(II)		II	II	II
III	III	(III)		III	III
IV	IV	IV	IV		
V	V	V	V		V
				VI	

other is due to the high conductivity, which has a large contribution to the spectra in the relevant temperature-frequency range. Due to practical problems, $\varepsilon''_{\mathrm{deriv}}$ could not be used to improve the result in this region.

4. DISCUSSION

We will focus the discussion on the processes II–VI. Process I is most likely related to conductivity and not so relevant in a study of confinement-induced supercooling. Also, it only shows up in Vycor.

It is always difficult from dielectric results alone to assign a process to a certain physical mechanism. We speculate not too much about the underlying physics but mainly use the absence or presence of a process in the different samples to reach a conclusion. The results are summarized in Table I.

Processes II, III, and VI seem to be indicating the presence of bulk ice. Processes IV and V are typical for the systems with confined water. The table can thus serve as a good guideline to compare the situation in the different samples. Process II is visible in all samples, except for the 74 and 29% samples. But for the case of 74%, we noted previously that we could not resolve the processes well enough and we might have missed process II. For the 29% sample, we did not access the temperature range where process II should appear. Although we cannot be entirely sure, there is no reason to believe that process II is really absent in the 74 and 29% samples.

Process III is clearly visible in all samples, except in the 29 and 13% ones. For the 29% sample, there is a process with an unclear relaxation time dependence at the edge of the range where the data were analyzed. This is probably process III, although we cannot be entirely sure. The 13% sample is the one with the lowest water content, and the amount of bulk-like ice may be very small such that a weak process as III maybe could not be observed. Summarizing, the occurrence of processes II and III indicates the presence of bulk-like ice in all systems, except for maybe the aerosils with very low water content, and in particular, the 13% one.

Processes IV and V are only present in the systems with confined water. This is evidence that the presence of a large surface area induces a substantial change in the dynamics of the water molecules. Moreover, the activation energy of processes III–V are quite alike. This indicates that IV and V have the same physical origin as III, but the structure of the water close to the surfaces is changed in such a way that this process is accelerated. This differs from our previous results on liquid crystals [8], where we found a surface-induced process retardation. But the liquid crystal was completely different from water, and the complex structure of water might be changed in such a way that near the surface an acceleration of the process is possible. The fact that there are two new processes in confinement might be an indication that there are three structures involved. For example, there could be a layer of molecules close to the surface where the dynamics is changed the strongest, giving rise to process V. The next layer then gives rise to the less altered process IV, and still further from the surface, the molecules have the structure of bulk ice.

The 333% water sample is the only sample where process V is present without process IV. It is not clear why process IV is absent here. Part of the explanation may be found in the fact that this sample is not dominated by the rigid structure of the Vycor glass or the compressed aerosil pellet.

Following the reasoning above for processes II and III, process VI should be visible in all samples. But it is already weak in bulk ice and might thus become undetectable when less bulk ice is present, as is the case in the confined samples. Another explanation can be that VI is the relaxation of water molecules in the liquid-like layer that is always present on an ice surface [14]. Of course, such a layer will be absent or substantially less developed for the case of the confined samples.

As a last point, we want to compare our results with those of the "2-H_2O vermiculite clay" from Ref. [5], since our processes IV, V, and VI appear to be related to the respective processes, 1, 2, and 3. The authors of Ref. [5] identify process 1 as resulting from "rather free" molecules, not bonded to the wall of the clay platelets. Process 2 is attributed to crystalline water in defects in the clay structure, where there is sufficient space for the water to crystallize. Also, the third process is probably related to a relaxation of water molecules in ice. We can support their claim concerning process 3 but not the other ones: we are confident that these processes are related to processes close to the surface. But we have to remark that the interaction with Na^+ ions in the clay can be significantly different from that with –OH groups in aerosils or with the Vycor surface.

Finally, when working with glass-forming substances, it is always interesting to verify the temperature dependence of the relaxation times. Water in confinement appears to have an Arrhenius temperature dependence ($\tau(T) = \tau_0 \exp(E/kT)$) [6]. Such a dependence shows as a straight line in plots of $\log \tau$ versus $1/T$. It can be seen from Figs. 2–4 that our results are in agreement with an Arrhenius dependence.

5. CONCLUSION

We have measured the dielectric response of samples of bulk and confined water below the melting point of water. We confined the water to Vycor porous glass and mixed aerosils with low and high concentrations of water. In these samples we observed a total of six processes and could separate out processes typical for bulk-like ice and for water close to the surface of the Vycor and the aerosils.

We observe the appearance of one new relaxation process in aerosils with a high concentration of water. For more strongly confined water, we found an extra new process. These processes are originating from a region close to the surface where the dynamics of the water is changed compared to bulk. Probably due to interaction with the –OH groups of the aerosils and an unspecified interaction with the Vycor surface, two new relaxations arise. We could not establish whether this surface layer is supercooled water or ice with a changed structure.

In all systems, except maybe for very low concentrations of water in aerosils, a fraction of the water, most likely located in the middle of the pores in Vycor and in between the aerosil particles, crystallizes to bulk-like ice.

It seems that within the experimental accuracy, all processes observed have an Arrhenius dependence.

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