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Dielectric study of supercooled 2D water in a vermiculite clay

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We report results of dielectric spectroscopy on water confined in a two-dimensional layer-structured Na-vermiculite clay. Several relaxation processes of different origin can be discerned in the spectra. A strong dielectric loss peak is observed in the clay with two layers of water molecules between the rigid clay platelets at temperatures between 125 and 215 K. This loss peak is neither observed in bulk ice, nor in the dry clay or clay with only one water layer between platelets. The relaxation time is shown to have an Arrhenius temperature dependence which does not extrapolate to the high-temperature behavior. This behavior is in accordance with the proposed so-called ''fragile-strong'' transition of supercooled bulk water, which implies a change in the temperature dependence of the relaxation time from a high-temperature non-Arrhenius to low-temperature Arrhenius behavior. However, this transition is experimentally elusive as it would occur in an inaccessible (due to the ease of crystallization) temperature range of the supercooled bulk water. © *2000 American Institute of Physics.* [S0021-9606(00)70225-X]

I. INTRODUCTION

The dynamics of bulk water has been extensively studied over a wide range of temperatures and pressures.[1–8] However, in many real systems water is not in its bulk form but located on surfaces or in small cavities. Such confined water makes up the main part of living organisms, and is essential for the functioning of all ''molecules of life'' over a wide range of temperatures, also well below the freezing point.[9]

Water is furthermore interesting from a scientific viewpoint due to its many peculiarities compared to other liquids, the most famous being the density maximum at 4 °C. The underlying reason for this anomaly and, in general, many of the other observed strange behaviors of water, is believed to originate in the strong hydrogen bonding between water molecules. Another of the more peculiar properties of water is the anomalous temperature dependence of many dynamical variables in the liquid and supercooled liquid state.[10] The temperature dependencies of the isobaric heat capacity, isothermal compressibility, density, diffusion coefficient, bulk and shear viscosity, sound velocity and absorption, and proton and oxygen spin-lattice relaxation times are all following the relation

$$P_i = P_i^0 (T/T_s - 1)^{\gamma_i}, \tag{1}$$

where P_i is the strongly temperature dependent physical property, $T_s = 228$ K, and P_i^0 and y_i are adjustable parameters.[10,11] The observation of power-law behavior is not new. In the case of viscosity, power-law behavior was reported as early as in the 19th century.[12] Thus, all these experimental techniques show evidence for some kind of thermodynamic transition at about 228 K. The reason for this critical behavior is not clear but it is a common feature for some theories. It is then not surprising that the dynamics of water has been discussed in terms of mode coupling theory (MCT) and percolation ideas.[13–16] In fact, MCT[17–19] predicts power-law behavior to be a general phenomenon common for viscous liquids, and, indeed, experimental data of a number of glass-forming systems show that high-temperature power-law behavior of, e.g., viscosity is quite general.[20]

Glass-forming systems generally show non-Arrhenius temperature behavior of the viscosity or the related time scale τ of the primary relaxation, the so-called α process. In Angell's classification,[21–23] covalently bonded systems with almost Arrhenius temperature dependence are denoted strong, while ionic and van der Waals systems, with highly non-Arrhenius behavior, are termed fragile.

Since the main α-relaxation time of the molecular motions extrapolates to infinity at T_s while the glass-transition temperature of water is generally accepted to be in the range 124–136 K,[24,25] the observed singularity indicates that some kind of dynamic phase transition must occur at a temperature around 228 K.[26] It has then been suggested that the temperature dependence of the α-relaxation time changes from a non-Arrhenius behavior at high temperatures to Arrhenius behavior at temperatures below T_s, i.e., a so-called ''fragilestrong'' transition occurs at T_s.[26] It has been proposed that this transition has a structural origin in which the supercooled water structure changes from its normal liquid structure to an amorphous hydrogen-bonded network.[26] The onset of the strong behavior, on decreasing temperature, around T_s, is then interpreted to be due to the end-point in the network formation process.

Since bulk water crystallizes in the temperature range 150–235 K,[27] it is not possible to experimentally verify the
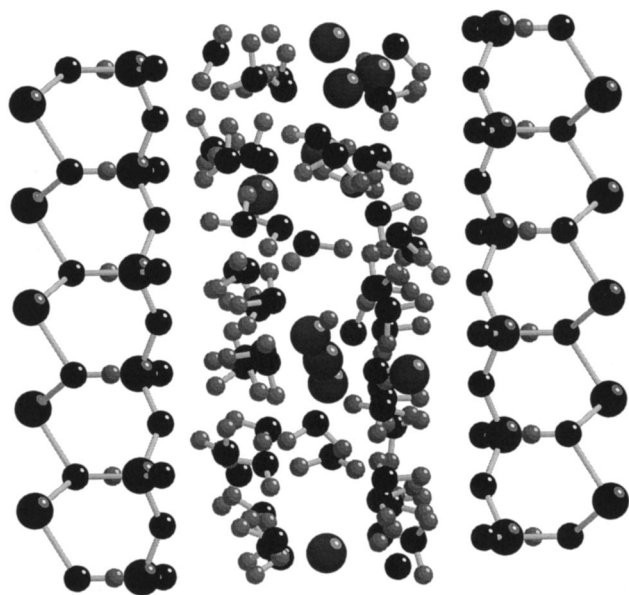
FIG. 1. Plausible molecular snapshot of the 2-H_2O layer Na-vermiculite clay based on neutron diffraction studies. The interplatelet water molecules are seen between two crystalline clay platelets. The larger spheres are the intercalated Na ions. The figure is taken from Ref. 43.

transition at 228 K for bulk water. Confined water, on the other hand, may provide a means to enter into this, for bulk water, inaccessible temperature region. Such studies have been performed[28] for water in pores which, therefore, are confined in all three dimensions. The results, obtained at a small temperature range above T_g, have indicated a fragile non-Arrhenius behavior also at lower temperatures for this confined supercooled water.[28] Thus, these results are in contradiction to the proposed ''fragile-strong'' transition.[26] Three-dimensional confinement has, however, been shown to speed up the α-relaxation of glass-formers.[29] It was also shown that this effect is less pronounced in systems confined in two dimensions. However, the cooperativity length does not depend on the dimensionality of the confinement.[29] This can be explained if we envisage the cooperativity region to be able to adapt its volume to the geometrical restrictions imposed. If this is true we would not expect large differences between an essentially two-dimensional (2D) system and its corresponding bulk material when it comes to the α-relaxation dynamics.

Na-vermiculite clay has a two-dimensional structure consisting of parallel clay platelets with intercalating adsorbed water and Na^+ ions in between platelets. The clay is able to adsorb water in well-defined amounts. Under ambient conditions there is one layer of water molecules between platelets while, in saturated conditions, there are two layers[30] (see Fig. 1). The water in the interplatelet space is thus, when considering microscopic motion, not confined in the, say, x and y directions, but only in the z direction, i.e., it is confined in only one dimension. As the interplatelet distance thus is very small and also contains the intercalated Na ions, the dynamics might be expected to be very different from bulk water. However, if the dynamics is mainly determined by the short-range hydrogen bonding, the 2D water in the

clay may be a model system that exhibits dynamics similar to bulk water.

Results from quasielastic neutron scattering on 2-H_2O layer hydrated Ca^{2+} montmorillonite clay show that the interjump residence time for the translational motion of the confined water indeed is similar to that of bulk water.[31] Our recent quasielastic measurements on the corresponding two-layer hydrated Na-vermiculite clay confirm this finding and indicate that the relaxational dynamics of such macroscopically extended water layers (typically 30 mm^2), with a thickness corresponding to two layers of water molecules (e.g., about 6 Å), is only slightly affected by the confinement.[32] However, despite the similar dynamics to bulk water we here show that most of the interlayer water is prevented from crystallization, and thus enables us to study the temperature dependence of the α-relaxation in the, for bulk water, inaccessible temperature region.

The main conclusion of the results has recently been published elsewhere,[33] where it was shown that the main relaxation of the deeply supercooled water in the fully hydrated Na-vermiculite clay exhibits an Arrhenius temperature dependence in accordance with the proposed ''strong'' nature of supercooled bulk water at low temperatures. We will here give a more elaborate account of these dielectric spectroscopy studies of water confined between platelets in the two-dimensional structure of Na-vermiculite clay.

II. EXPERIMENT

The vermiculite crystals were from Eucatex, Brazil. Crystals 0.3 mm thick and about 30 mm^2 in area were washed and then treated for about a year with 1 M NaCl solution at 50 °C, with regular changes of solution, to produce a pure Na vermiculite, with the chemical formula[34]

$$Si_{6.13}Mg_{5.44}Al_{1.65}Fe_{0.50}Ti_{0.13}Ca_{0.13}Cr_{0.01}K_{0.01}O_{20}(OH)_4Na_{1.29}.$$

Vermiculites and smectites are unique in the sense that they are able to provide two-dimensional geometries with extremely thin and well-defined thickness of the water layer. The reason for this is that the interlayer cations have a strong tendency to hydrate and thereby force the clay layers apart in a series of discrete steps.[30] A totally dry Na-vermiculite crystal has a spacing between two consecutive clay layers (d-spacing) of approximately 10.6 Å. This d-spacing increases to 11.78 Å for a relative humidity up to about 70% and to 14.96 Å for a relative humidity above 70%.[30] If one subtracts the thickness of the rigid clay platelets there remains about 2 Å (i.e., the diameter of Na^+) for the sodium ions in the dry 10.6 Å phase, about 3.2 Å (corresponding to one layer hydrate) in the 11.78 Å phase, and approximately 6.4 Å (corresponding to two layer hydrate) in the 14.96 Å phase. Thus, the thickness of the water layer can be regulated very accurately simply by varying the relative humidity.

In our case we produced a totally dry Na-vermiculite by drying the clay at 100 °C in a vacuum oven. The 2-H_2O layer clay was submerged in water and after removing surface water put directly into the sample container. The 1-H_2O layer sample was prepared by leaving the 2-H_2O layer clay to dry in ambient conditions with a relative humidity
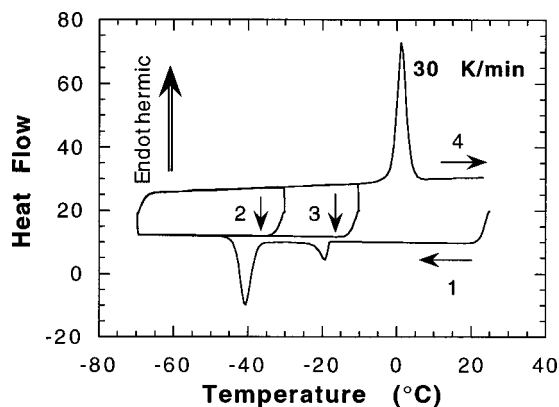
FIG. 2. Typical DSC trace of the 2-H_2O layer Na-vermiculite clay. The scan rate was 30 K/min. Starting at ''1'' the numbered arrows indicate the history of the trace.

($\approx 50\%$) corresponding to one layer hydration. The hydration was carefully monitored by weighing the samples.

In the case of the Na-vermiculite from Llano Texas,[30] there are an average of 2.1 water molecules per interplatelet Na^+ ion in the 11.78 Å phase, and all the hydrogen atoms are directed toward the adjacent clay platelets.[30] The situation is very different in the 14.96 Å phase, where there are, on average, 4.9 water molecules per interplatelet Na^+ ion, and only about half of these water molecules are oriented so that they can form a hydrogen bond to one of the clay surfaces, see Fig. 1.[30] It should be noted here that since we are using a Na-vermiculite from Eucatex Brazil, with a lower charge density of the clay platelets, there should be slightly more water molecules per interlayer Na^+ ion in our case.

Differential scanning calorimetry (DSC) (Perkin Elmer, Pyris 1) was performed on the two-H_2O layer clay using scan rates of 2 to 40 K/min. Samples with different weights (typically 20–60 mg) of clay were prepared and then measured during several different temperature cycles.

Samples for the dielectric study were prepared by placing pieces of Na-vermiculite clay sheets between gold plated stainless steel parallel-plates (diameter=20 mm). The applied electric field ($\approx 1\,V$) is thus perpendicular to the clay

platelets and water layers. Samples with water content corresponding to 0-, 1- and 2-H_2O layers between clay platelets were prepared with thicknesses in the range of 0.25–0.45 mm. Each sample thus consists of hundreds of thousands of water layers in parallel. A sample of bulk water was also prepared for reference.

The dielectric measurements were performed on a high resolution Novocontrol system (Alpha) covering a broad frequency range (10^{-2}–10^7 Hz) over the temperature range 120–300 K. Isothermal (within ± 0.02 K) frequency (f) scans of the complex dielectric function, $\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f)$, were performed every third degree.

III. RESULTS

A. Differential scanning calorimetry

A representative DSC trace on the 2-H_2O layer clay is shown in Fig. 2. Two exothermic peaks are easily observed. The magnitude of the peak at $\approx -20\,°C$ is readily decreased by drying the surface of the sample. We therefore attribute this peak to crystallization of surface water. The magnitude of the peak at $\approx$-40 °C is unaffected by such treatment and we believe this peak is due to partial crystallization of the interplatelet water presumably residing in defects or voids of the clay. To calculate the amount of water that crystallizes, we use the heat of fusion at 0 °C and the estimation by Angell *et al.*[35] that 30% of that is lost at -40 °C. We then find that approximately 24% of the water crystallizes. Thus most of the interplatelet water molecules do not crystallize but remain in a supercooled liquidstate, also in the temperature range referred to as ''no-mans land'' for bulk water.[15]

B. Dielectric spectroscopy

In Fig. 3 we show three-dimensional plots of the frequency and temperature dependence of the measured dielectric loss, i.e., the imaginary part of the permittivity. While the dielectric response of the 1-H_2O layer clay is rather featureless, a strong and broad dielectric loss is observed in the 2-H_2O layer clay. It is clearly moving to higher frequencies, f, with increasing temperature. The peak in $\epsilon''(f)$ of the
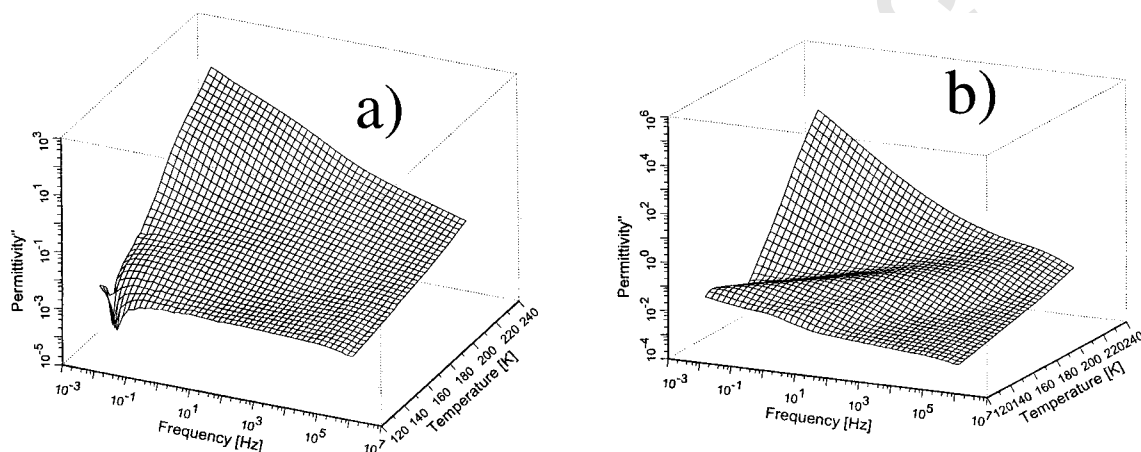

FIG. 3. Three-dimensional representation of the temperature and frequency dependence of the imaginary part $\epsilon''(f)$ of the dielectric function $\epsilon^*(f)$ of the Na-vermiculite clays: (a) 1-H_2O layer clay and (b) 2-H_2O layer clay.
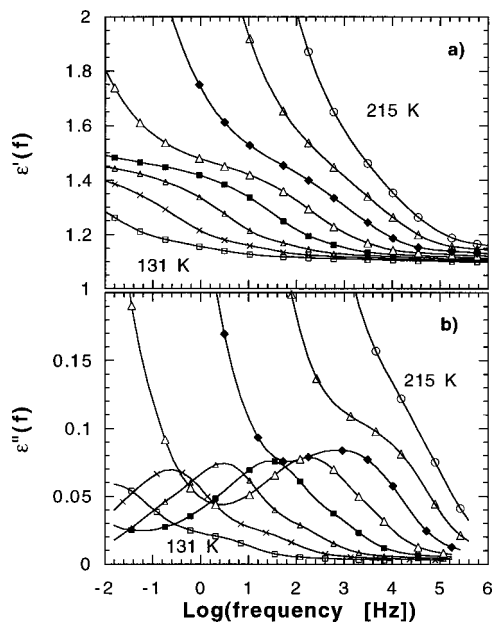
FIG. 4. Frequency dependence of the real part $\epsilon'(f)$ (a) and of the imaginary part $\epsilon''(f)$ (b) of the dielectric function $\epsilon^*(f)$ of the 2-H_2O layer Na-vermiculite clays at some of the measured temperatures. Spectra shown from left to right were recorded at 131 K and every twelfth degree until 215 K.

2-H_2O layer clay can be observed in the temperature range 125–215 K, see Fig. 4. When it enters at the low-frequency side of our dynamical window at the lowest temperatures, the peak is bimodal and at the highest temperatures the, by now monomodal, peak is swamped by a low-frequency dispersion. Figure. 5 shows the imaginary part of the dielectric response of the clays with 0-, 1-, and 2-H_2O layers between platelets at 185 K. Clearly, the loss peak observed in the 2-H_2O layer clay is absent in the clays with less water. The $\epsilon''(f)$ spectrum of the 2-H_2O layer clay in Fig. 5 is well described (solid line) by a sum of a power law and a Cole-Cole function,[36]

$$\epsilon''(\omega) = \frac{\sigma_{DC}}{\epsilon_0}\omega^{-n} + \mathrm{Im}\left[\frac{\Delta\epsilon}{1+(i\omega\tau)^\alpha}\right]. \quad (2)$$

In this equation $\omega = 2\pi f$, $\Delta\epsilon = \epsilon_s - \epsilon_\infty$, where ϵ_s and ϵ_∞ stand for the static and high-frequency limiting values of the
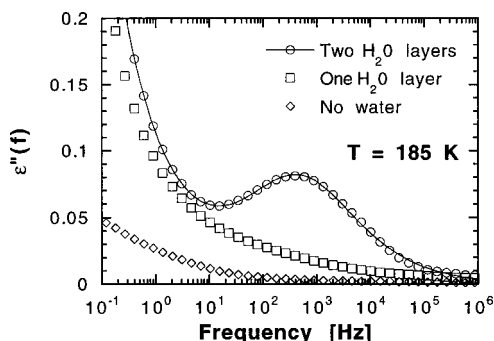

FIG. 5. Frequency dependence of $\epsilon''(f)$ of the Na-vermiculite clays at 185 K. The line through the data points of the 2-H_2O layer spectrum is a least square fit to a superposition of a power law (conductivity) and the imaginary part of a Cole-Cole function (relaxation).
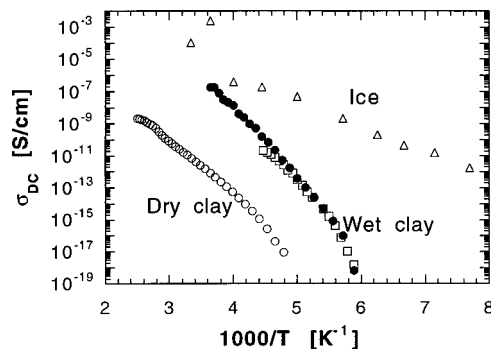

FIG. 6. Temperature dependence of the conductivity parameter as obtained from fitting the low-frequency dispersion. The values for the 1- (open squares) and 2-H_2O layer clays (filled circles) are very similar. For comparison also the results for the dry clay (open circles) and bulk water or ice sample (open triangles) are shown.

dielectric constant, respectively, while τ is the relaxation time. At the lower temperatures we have to use at least two Cole-Cole functions to account for the bimodal shape. At the lowest temperatures it seems as if there is a further very small broad contribution in addition to the main and second peaks. In the following we will first account for the strong low-frequency dispersion of the samples and then, for each sample separately, the relaxational processes observed.

1. The low-frequency dispersion

The low-frequency dispersion is well described by the conductivity term of Eq. (2), where σ_{DC} is the conductivity and ϵ_0 is the permittivity of free space. However, it is questionable if the observed dispersion is due to normal conductivity, as this dispersion is also observed in the real part of the permittivity. Also, the low value of the exponent n (see inset of Fig. 6) suggests a different underlying mechanism for this dispersion.

Figure 6 shows the temperature dependence of the σ_{DC} parameter for the different clays as obtained from least squares fits. It is remarkable that the behavior of the 1- and 2-H_2O layer clays is almost identical. This implies a connection of the low-frequency dispersion to the Na-ions or water molecules with bondings to the internal surfaces of the clay platelets. Note that no discontinuity can be seen in the measured temperature range for the σ_{DC} parameter in the clays. The geometry of the sample suggests the low-frequency dispersion, or imperfect conduction, to be explained in terms of collective polarization of charge carriers within each inter-platelet space.

2. The dielectric loss of the 2-H_2O layer clay

From Fig. 4 it is clear that at least two relaxation processes contribute to the low-temperature spectra. In fact, three peaks can be identified at the lowest temperatures, see Fig. 7. However, the third peak is difficult to resolve due to its low amplitude and broad shape. Furthermore, it is close to the high-frequency limit of the equipment. Therefore the fit parameters for this third peak are inflicted with large uncertainties and should be analyzed with great care.

The relaxation strengths, $\Delta\epsilon$, of the processes as obtained from the fits are shown in Fig. 8. It is seen that while
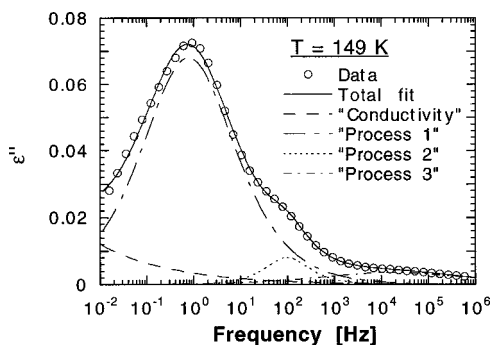
FIG. 7. Frequency dependence of $\epsilon''(f)$ of the 2-H$_2$O layer clay at 149 K. The line through the data points is a least square fit to a superposition of a power law (dashed line) and the imaginary part of three Cole-Cole functions. Each Cole-Cole contribution is also shown separately.

FIG. 9. Temperature dependence of the shape parameters α of the processes in the 2-H$_2$O layer clay.

the much stronger main process has an almost temperature independent relaxation strength, the weaker processes observed at higher frequencies have strengths that decrease with increasing temperature. Therefore, at $T > 175$ K we observe a monomodal shape of the loss peak until at yet higher temperatures the loss is swamped by the strong low-frequency dispersion, see Figs. 3 and 4.

The shapes of the processes as parametrized by the parameter α of Eq. (2) are shown in Fig. 9. For completely free fits to one as well as to three Cole-Cole processes to the dielectric loss, the value of α for the main process shows a slightly increasing trend for decreasing temperature at the lowest temperatures. However, this trend is accompanied by a downward trend for the α-parameter of the second peak, leading us to attribute these trends to compensation effects in the fitting procedure. It is then to be noted that this occurs in a temperature range where the main peak is not fully inside the dynamical window of the spectrometer. It is reasonable to assume, from the data at higher temperatures, that the second peak is of a true Debye type ($\alpha = 1$). At these and even higher temperatures, where only one peak can be resolved in the data, the broadening of the main process seems to have a slight tendency to increase with increasing temperature. A similar behavior is observed for the very broad third process of very low dielectric strength.

In Fig. 10 we show the obtained relaxation times together with some literature data for both bulk and confined water. The main dielectric relaxation of the 2-H$_2$O layer clay follows an Arrhenius behavior with an activation energy of
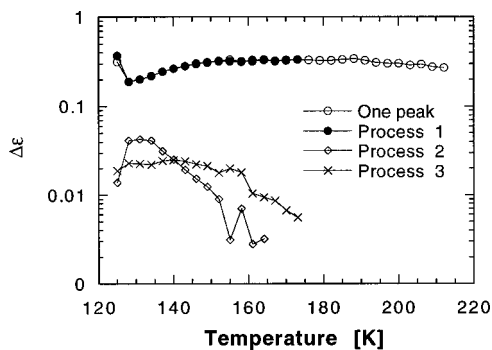
0.42 eV, while the second dielectrically much weaker process has an activation energy of 0.34 eV. The results from the third process are rather scattered due to the above mentioned difficulties for the analysis. However, a fit through the scattered data gives an activation energy of ≈ 0.25 eV. It is then important to note that two processes with activation energies very similar to that found for the second and third process were also observed in our reference sample of crystalline water. The main process, however, was exclusively observed in the 2-H$_2$O layer clay.

3. The dielectric loss of the 1-H$_2$O layer clay

The strong loss due to the main process in the 2-H$_2$O layer clay is clearly absent in the 1-H$_2$O layer clay (see Fig. 3). However, at low temperatures (below 180 K) a very small
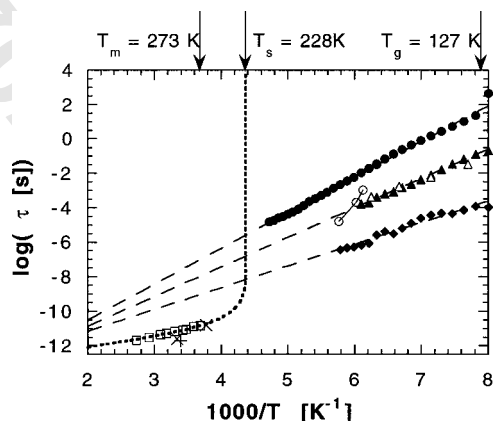
FIG. 10. Relaxation times obtained from fits of the dielectric and neutron scattering spectra from the 2-H$_2$O layer clay together with literature data. The filled circles denote the relaxation times for the main dielectric relaxation and the filled triangles show the relaxation time of the second process observed at low temperatures. The filled diamonds denote the relaxation time of the weak third process. The dashed straight lines are fits to the Arrhenius equation, $\tau = \tau_0 \exp(E/RT)$, to the relaxation times of the three processes. The open triangles coinciding with the relaxation times of the second process are from Cole-Cole fits of our dielectric spectra of bulk ice. Also included are new literature data (open squares) of the dielectric relaxation time of bulk water at higher temperatures (Ref. 4). The dotted line through the data is a power law (exponent $= -1.55$) diverging at $T_s = 228$ K as proposed in the literature (Ref. 10). The residence times of the neutron scattering data of our system (X) (Ref. 32) coincide with the neutron scattering data (+) (Ref. 31) and the dielectric relaxation times data of bulk water. The data points (open circles) at lower temperatures are from dielectric measurements on water sequestered in pores of a polymer matrix (Ref. 28).

FIG. 8. Temperature dependence of the dielectric relaxation strengths of the different processes observed in the 2-H$_2$O layer clay.
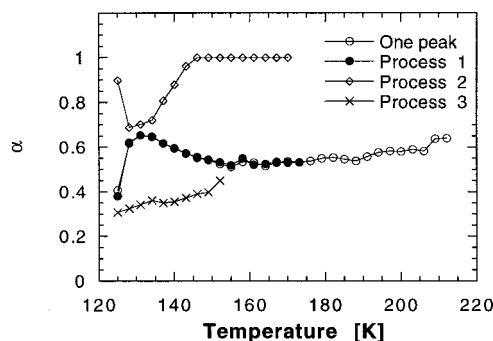
loss can be discerned also in the 1-H_2O layer clay. This peak can be fitted by a broad Cole-Cole function with a relaxation time that follows the temperature behavior of the weakest and fastest relaxation found in both ice and the 2-H_2O layer clay. Neither the somewhat stronger relaxation (process 2) observed in both ice and the 2-H_2O layer clay nor the main process of the 2-H_2O layer clay can be detected. Thus, the 1-H_2O layer clay does not contain water molecules that can relax through the process giving rise to the main peak in the 2-H_2O layer clay. Furthermore, the absence of process 2 indicates that no crystalline water is present in the 1-H_2O layer clay. Since there are water molecules without any bonds to the platelet walls in the 2-H_2O layer clay and not in the 1-H_2O layer clay, we attribute the main process of the 2-H_2O layer clay to the dipolar relaxation due to the reorientation of these ''rather free'' molecules.

4. The dielectric loss of the 0-H_2O layer clay

The only process, apart from the low-frequency dispersion, that can be observed in the dry 0-H_2O layer clay is a weak loss at a temperature range between 220 and 320 K. This is at considerably higher temperatures than those where processes 1-3 in the wet clays were observed. The weak loss peak can be fitted with a Cole-Cole function with a temperature independent α-parameter (≈ 0.4) and a relaxation time that follows an Arrhenius temperature dependence, see Fig. 10. The activation energy of this process is found to be $E_A \approx 0.7$ eV, which is much higher than found for any of the processes (1-3) observed in the wet clays. The physical origin of this process is not understood at present but it is clear that it can not be observed in the wet clays. This is probably due to the strong low-frequency dispersion in the wet clays which swamps any other high-temperature feature. It is important to note that there is no relaxation peak observed in the dry clay at the temperature range of interest for the investigation of water dynamics in the wet clays.

IV. DISCUSSION

Let us first discuss the failure of total crystallization of water in the 2-H_2O layer clay. Clearly, the space between clay platelets in 2-H_2O layer clay seems to be too small to allow for crystallization. The only form of ice that would fit would be a bilayer crystal of the form found in a simulation for TIP4P water.[37] However, we believe that the presence of sodium ions introduces the disorder necessary to prevent total crystallization of the interlayer water. Partial nucleation may then probably occur in small regions relatively far from neighboring sodium ions or in larger voids formed by structural defects of the clay platelets. Our differential scanning calorimetry measurements show that approximately 24% of the interlayer water in the 2-water layer system crystallizes at ≈ 235 K, whereas the remaining water remains in a supercooled ''liquid'' state. The structure of this mixture of crystalline and supercooled water will be investigated by neutron diffraction in the near future.

We now turn to the observations made in the dielectric spectra. We start by discussing the strong low-frequency dispersion which is the main feature of the spectra of all clays.

It can be described by a powerlaw which suggests that it could be attributed to conductivity. However, as this powerlaw is accompanied by a similar powerlaw also in the real part of the permittivity, and also considering the sample geometry, this explanation seems unlikely. We instead attribute this dispersion to the so-called anomalous low-frequency dispersion as treated by Jonscher.[38,39] Interestingly, the powerlaw dispersion at low frequencies is identical in the 1- and 2-H_2O layer clay over the whole studied temperature range. This suggests that this process is due to a macroscopic polarization originating in the hindered motion of the hydrated Na-ions. In the 0-H_2O layer clay the process is much weaker and this difference may be related to the fact that the Na-ions are not hydrated in the dry clay.

Although we can distinguish three separate Arrhenius processes in the spectra of the 2-H_2O layer Na-vermiculite clay, its dynamics is dominated by the main and slowest process. The two faster processes are much weaker and will here be treated in less depth and we concentrate on the main process.

It is to be noted that the relaxation times of process 2 of the 2-H_2O layer clay coincide, within the experimental accuracy, with the relaxation times we obtain for ice, see Fig. 10. We therefore attribute this process to regions of crystalline water at the surface or in structural defects of the rigid platelets. Since ice has been reported to have multiple relaxations it is possible that also the third and fastest process (process 3) have the same origin. It is then important to note that the weak process 3 observed in the 1- and 2-H_2O layer clay is observed also in ice, but found to be much broader in the clays. This process may therefore be attributed to some very local process such as reorientation of molecules realized by motion of Bjerrum type defects[40] in ice, however, in the case of the clays occurring in a disordered environment. Clearly, more studies are needed to resolve this issue.

After having addressed the small secondary peaks we will in the following motivate our assignment of the main peak in the 2-H_2O layer clay to amorphous water in the clay. The very high amplitude, which tells us that most of the dipoles relax via this process, combined with the fact that the DSC measurements showed that there is substantially more amorphous water than crystalline water in our 2-H_2O layer clay, strongly suggests that the main process is due to relaxation of supercooled or amorphous water.

The calorimetric glass-transition temperature T_g corresponds to the temperature for which the relaxation time is ≈ 100 s. It is then interesting to note that the main relaxation process in the 2-H_2O layer clay has a relaxation time of 100 s at 127 K which is close to the T_g of bulk water.[24,25] This suggests that the dynamics is rather bulklike also at low temperatures. It is also highly non-Debye, the fractional exponent α of the Cole-Cole function being close to 0.5, see Fig. 9. This can be explained by identifying this process to the reorientation of water molecules in a disordered network. As the process is only seen in the 2-H_2O layer system, we attribute this process to the reorientation of confined water molecules that are not directly interacting with the clay walls.

The low-temperature Arrhenius behavior of the main

process does not extrapolate to the characteristic times obtained from quasielastic neutron scattering (QENS) data at higher temperatures, see Fig. 10. The QENS data were obtained from a jump diffusion model fitted to the Q-dependence of the width of the quasielastic broadening.[32] The dielectric relaxation times are expected and found to be somewhat slower than the residence time found from QENS data because the dipoles are likely to relax to their new equilibria via several jumps.

We conclude that there is a clear difference in the water dynamics at high and low temperatures in the 2-H_2O layer clay. From our data it thus appears as if a crossover in the temperature dependency of the dynamics must occur in the temperature range 215–265 K. Above this temperature range the dynamics is strongly non-Arrhenius,[32] which is characteristic for a fragile glass-former in Angell's classification,[21–23] whereas at lower temperatures, below 215 K, the dynamics follows an Arrhenius behavior as for the strong glass-formers. Thus, the present data suggest the presence of a phase transition between strong and fragile behavior as recently suggested for bulk water by Angell.[26] In this context it is interesting to note that NMR studies have shown that a slow in-plane rotation of the hydrated Na-ions freezes in over this temperature range.[41] This observation can be attributed to the completion of a hydrogen-bonded network of the intercalated water which also explains the crossover to ''strong'' behavior at low temperatures.

It is extremely interesting that this highly confined water behaves so similar to bulk liquid water at both high and low temperatures when it comes to the main relaxation time. The explanation is probably related to the fact that this 2D water is confined in only one dimension. The dynamics may then have enough space to have the same degree of cooperativity as in the bulk case since there is a possibility of interacting over large distances in the plane. This would not be the case for water in pores which are confined in all three dimensions.

These findings may also be of importance for understanding water dynamics in biological systems, since in biology water often exists in confined geometries similar to the one studied here.[42]

V. CONCLUSION

The dielectric response of water confined in the interplatelet space of a Na-vermiculite clay shows a low-temperature broad loss-peak with an Arrhenius temperature dependence. There seems to be a crossover from non-Arrhenius to Arrhenius temperature dependence in this confined water at a temperature not too far from where a ''fragile-strong'' transition has been proposed for bulk water.[26] This can be explained by the formation of a hydrogen-bonded network that turns the 2-H_2O layer system into a strong network glass-former at low temperatures.

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