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Water under inner pressure: A dielectric spectroscopy study

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Water is the most studied substance on Earth. However, it is not completely understood why its structural and dynamical properties give rise to some anomalous behaviors. Some of them emerge when experiments at low temperatures and/or high pressures are performed. Here we report dielectric measurements on cold water under macroscopically constrained conditions, i.e., water in a large container at constant volume that cannot freeze below the melting point. The inner pressure in these conditions shifts the α relaxation peak to similar frequencies as seen in ice Ih. At 267 K we observe a peculiar response possibly due to the Grotthuss mechanism. At 251 K (the triple point) ice III forms.

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I. INTRODUCTION

Since the seminal works of Canton *et al.* in the 18th century [1,2], water has been extensively studied to understand its structure and dynamical behavior. Due to its small molecular size, its polarity, and, most important, the interaction through hydrogen bonds, water exhibits many special properties. Most authors agree to call such properties anomalous [3,4], and a sophisticated phase diagram is evidence of it [5]. Water has 11 stable triple points and remarkable versatility in forming crystalline structures, like no other known substance [4,6]. Upon freezing, water molecules rearrange themselves to occupy either more volume (ice lh) or less (for example, ice III), depending on whether pressure exceeds that of the minimum in the melting temperature (209.9 MPa).

Below 273 K, water can exist in a liquid state in precarious equilibrium. Indeed, when it is cooled around 10^6 K/s, freezing can be avoided, and water remains in a supercooled state until it turns into a glassy state [7–9]. On the other hand, stable crystalline phases are usually obtained by pressure applying different methods at low temperatures [10–16]. In particular, ice III is generally obtained in three different ways: cooling the liquid at about 300 MPa, warming ice II at about 300 MPa, or decompressing ice V at about 247 K [10].

Dielectric spectroscopy has proven to be a powerful technique to investigate the molecular behavior of water, particularly because the relaxation times provide information about the cooperative processes, proton mobility, viscosity of the medium, and, in general, structural properties of the molecular network [14,17,18]. This is the technique we use in the present article, where dielectric measurements of water at low temperatures and constant (constrained) volume are performed. At these conditions, as we decrease the temperature, the pressure increases strongly. This internal pressure shifts the Debye relaxation to lower frequencies, as in the case of ice Ih. At temperatures below 251 K, the relaxation times deviate and slightly increase, possibly due to the formation of thin shells of ice III and Ih.

Many works have been carried out to study water in confined conditions to explore the inaccessible temperature zone for bulk supercooled water, especially in very fine glass capillaries and nanoporous materials. The study of the "fragile-strong" phase transition of this confined water and the effect produced by the boundaries and distances between them (around 1 nm to 20 μm) has also attracted the interest of researchers [19–26].

In the present work our aim is to study water confined in a macroscopic metallic container.

II. EXPERIMENT

Our measurements were carried out in a tight and long cylindrical capacitor able to endure inner pressures as high as 200 MPa. The central piece of the setup is a stainless steel cylindrical capacitor 15 cm in length, consisting of an inner electrode with a diameter of 0.47 cm separated 0.23 cm from the outside electrode. This latter electrode is 0.6 cm thick. The capacitor is surrounded by an aluminum block with channels where antifreeze (dynalene HC-50) flows through in order to lower the temperature. The aluminum block not only sets the working temperature but also acts as a Faraday cage to isolate the capacitors and connectors from the outside environment. The electrodes are connected with a copper wire to BNC connectors located on the outside of the block [27]. Two different experiments were performed. In the first one, the capacitor was totally filled with 6.87 mL of water (Mili-Q, 18.2 MΩ cm) and sealed with two rigid nylon caps that are screwed to the outer electrode. This volume is the total volume of the capacitor, and care was taken to remove bubbles. In the second experiment, 90% of the total volume was poured inside the capacitor, which was cooled down to freezing until water expanded to fill the remaining volume and was then sealed. The dielectric variables, ϵ' and $\tan\delta$ ($\tan\delta = \epsilon''/\epsilon'$), were measured using an LCR meter (HP 4284A) in the frequency interval 10^2 to 3×10^5 Hz. The temperature of the device was controlled by a PolySciences circulating bath from 277 to 239 K in steps of 2 K, with a thermal stability of ± 0.1 K. In order to get thermal equilibrium in the whole capacitor, the experiments were performed 1 h later for each temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the relative permittivity as a function of frequency for water [Fig. 1(a)] and ice Ih [Fig. 1(b)] at different temperatures. The main aim of this work was to

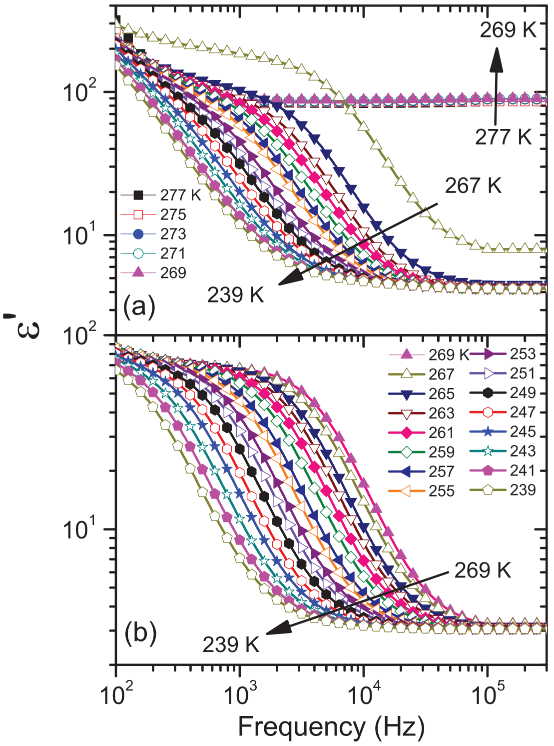

FIG. 1. (Color online) Relative permittivity as a function of frequency from 277 to 239 K in steps of 2 K for (a) water and (b) ice Ih. The symbols are the experimental data, and the lines are the fits as described in the text. The isothermals in (a) (from 267 to 239 K) are labeled in (b).

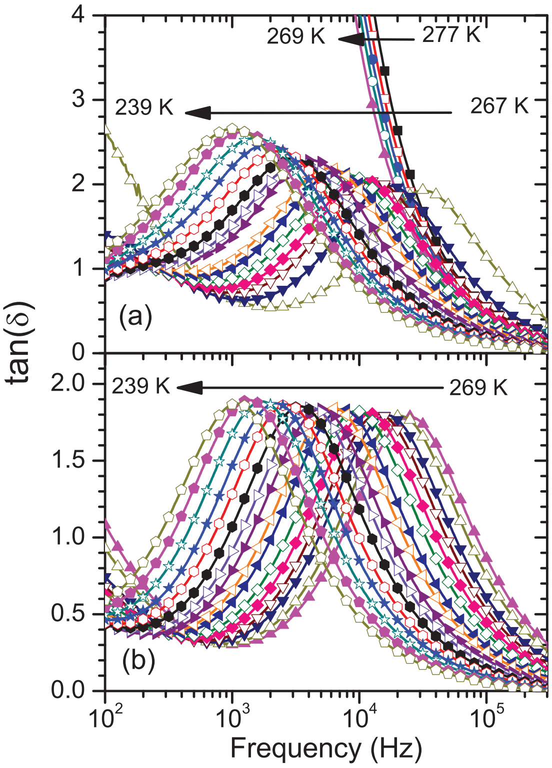

FIG. 2. (Color online) Dielectric loss tangent as a function of frequency from 277 to 239 K in steps of 2 K for (a) water and (b) ice Ih. The nomenclature of the symbols is shown in Fig. 1. The symbols are the experimental data, and the lines are the fits as described in the text.

study the behavior of the water, but we show the results of ice Ih (a phase well studied before [11,13,14,28], although not as systematically as reported here) for comparative purposes. Figure 1(a) shows the usual dielectric response of water from 277 to 269 K, composed of a region of a very high relative permittivity at the lowest frequencies, caused by electrode polarization, and a second region where the dipole response gives a flat contribution corresponding to the static value of ϵ'. From 267 to 239 K the Debye relaxation moves to lower frequencies as the temperature decreases. Note that an intriguing response occurs at 267 K: it separates significantly from the rest of the curves. This very reproducible response is puzzling because, normally, electrode polarization fades away at frequencies below or around 10^3 Hz due to the fact ions have a slow diffusion and cannot respond to faster electric fields. However, in Fig. 1 it is clear that ϵ' is greater than 100 even at 10^4 Hz. Dipoles cannot be the source of this high response; therefore, we need to explain this effect using an ionic mechanism, which will be explained at the end of the paper.

Although the dielectric loss signal is normally given by the imaginary part of the complex dielectric function, we prefer to plot $\tan\delta$ in order to highlight the details of the main relaxation peak (see Fig. 2). Again, there is a clear distinction between the response obtained at 267 K and those found at lower temperatures. Moreover, while the maximum amplitudes of ice Ih are quite the same regardless of the temperature, for water they increase as the temperature decreases.

The dielectric spectra of Figs. 1 and 2 (ϵ' and $\tan\delta$) were fitted using Havriliak-Negami equations [29,30]:

$$\epsilon^* = \epsilon'_\infty + \frac{\Delta\epsilon_{EP}}{(1+2\pi i f \tau_{EP})^{\beta}} + \frac{\Delta\epsilon_{\alpha}}{(1+(2\pi i f \tau_{\alpha})^{\delta})^{\gamma}} + \frac{\sigma_{dc}}{2\pi i f \epsilon_0}, \tag{1}$$

where EP stands for electrode polarization, α stands for Debye relaxation, and σ_{dc} is the dc conductivity.

In Table I we present the fitting parameters found using Eq. (1) for water under pressure at various temperatures. The parameters β and δ are not included because they do not change appreciably with temperature. The mean values are $\beta = 0.8232 \pm 0.0017$ and $\delta = 0.9502 \pm 0.0014$. In contrast, the exponent γ exhibits a peculiar behavior; first, it is slightly greater than 1 and does not change with temperature, and then it has a noticeable increment below the triple point. Figure 3 shows the dielectric relaxation times obtained from such fits versus the reciprocal temperature for water and ice Ih. The relaxation times for water are similar to the ones reported for ice Ih [12,14,31–33], but they start to separate at 251 K. In order to understand this behavior, see Fig. 4, which depicts the water phase diagram for pressures below 10^3 MPa [5] in the temperature range of this work. It is evident that, as the liquid is cooled below 273 K, the thermodynamic path follows the coexistence line where the pressure climbs to very high values.

TABLE I. Fitting parameters obtained using Eq. (1) for water under pressure at various temperatures.

T (K)	$\Delta\epsilon_{EP}$	$\Delta\epsilon_{\alpha}$	τ_{EP}	τ_{α}	γ
267	599.58 ± 725	168.69 ± 1.5	$6.71 \times 10^{-3} \pm 7.4 \times 10^{-3}$	$2.15 \times 10^{-5} \pm 5.34 \times 10^{-7}$	1.2 ± 0.1
265	399.35 ± 32.8	92.50 ± 1.11	$3.63 \times 10^{-3} \pm 3.12 \times 10^{-4}$	$4.21 \times 10^{-5} \pm 4.47 \times 10^{-7}$	1.107 ± 0.013
263	444.18 ± 18.6	83.38 ± 0.77	$3.63 \times 10^{-3} \pm 1.6 \times 10^{-4}$	$5.49 \times 10^{-5} \pm 3.41 \times 10^{-7}$	1.137 ± 0.007
261	507.04 ± 20	81.61 ± 0.78	$3.78 \times 10^{-3} \pm 1.5 \times 10^{-4}$	$6.73 \times 10^{-5} \pm 3.85 \times 10^{-7}$	1.156 ± 0.006
259	425.31 ± 13.6	80 ± 1.23	$3.05 \times 10^{-3} \pm 1.08 \times 10^{-4}$	$8.43 \times 10^{-5} \pm 7.68 \times 10^{-7}$	1.165 ± 0.009
257	463.34 ± 14.9	79.80 ± 1.33	$3.15 \times 10^{-3} \pm 1.08 \times 10^{-4}$	$1.05 \times 10^{-4} \pm 1.06 \times 10^{-6}$	1.185 ± 0.009
255	498.98 ± 15.2	79.00 ± 1.25	$3.3 \times 10^{-3} \pm 1.04 \times 10^{-4}$	$1.19 \times 10^{-4} \pm 1.27 \times 10^{-6}$	1.21 ± 0.01
253	543.4 ± 20.4	77.99 ± 1.46	$3.52 \times 10^{-3} \pm 1.31 \times 10^{-4}$	$1.59 \times 10^{-4} \pm 2.56 \times 10^{-6}$	1.267 ± 0.017
251	430.36 ± 13.1	83.24 ± 2.02	$2.9 \times 10^{-3} \pm 9.72 \times 10^{-5}$	$2.08 \times 10^{-4} \pm 4.35 \times 10^{-6}$	1.233 ± 0.024
249	396.28 ± 14.1	88.60 ± 3.45	$2.65 \times 10^{-3} \pm 1.05 \times 10^{-4}$	$2.63 \times 10^{-4} \pm 6.68 \times 10^{-6}$	1.16 ± 0.03
247	481.71 ± 23.9	91.01 ± 2.49	$3.32 \times 10^{-3} \pm 1.76 \times 10^{-4}$	$3.25 \times 10^{-4} \pm 9.04 \times 10^{-6}$	1.291 ± 0.048
245	405.68 ± 12.6	83.55 ± 2.64	$2.81 \times 10^{-3} \pm 1.07 \times 10^{-4}$	$4.17 \times 10^{-4} \pm 9.33 \times 10^{-6}$	1.154 ± 0.041
243	588.33 ± 71	105.46 ± 8.27	$4.37 \times 10^{-3} \pm 5.13 \times 10^{-4}$	$5.51 \times 10^{-4} \pm 1.41 \times 10^{-5}$	1.39 ± 0.08
241	450.17 ± 25.4	101.68 ± 13.5	$3.72 \times 10^{-3} \pm 3.1 \times 10^{-4}$	$7.05 \times 10^{-4} \pm 3.13 \times 10^{-5}$	1.4 ± 0.1
239	421.2 ± 38.1	172.51 ± 66.9	$4.33 \times 10^{-3} \pm 8.33 \times 10^{-4}$	$1.07 \times 10^{-3} \pm 1.82 \times 10^{-4}$	1.631 ± 0.115

Indeed, according to the Clausius-Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}, \tag{2}$$

where P, T, H, and V are the pressure, temperature, enthalpy, and volume, respectively, the pressure augments considerably against the electrodes due to the fact the volume is not allowed to increase ($\Delta V = 0$). As a matter of fact, it can be observed in Fig. 1 that around 267 K a phase transition occurs. However, this transition cannot be from liquid to ice Ih because in order to form, ice Ih needs to expand. Since the volume and mass are constant, the density cannot change. Therefore, according to the phase diagram, the sample remains liquid until approximately 210 MPa (at 251 K), when the triple point is reached. This coincides with the deviation shown in Fig. 3. At this point, a shell of ice III starts to nucleate on the electrode surfaces by the high pressure pushing against them. Furthermore, due to the fact ice III is denser than water, as soon as it appears, it leaves space for a thin layer of ice Ih to form. In the inset of Fig. 3 we show a schematic of this situation. Obviously, liquid water must necessarily remain in the interior to exert the pressure ice III needs to exist.

The relaxation times shown in Fig. 3 have an Arrhenius behavior. One could think that this is natural due to the fact that both phases coexist. However, it is not at all easy to see how the relaxation times of water are around 8 orders of magnitude greater than normal water [34–37]. It is plausible to explain such an outcome if we draw upon previous works [38,39]. There, it is stated that when water is compressed at very high pressures, the molecules increase the number of near neighbors, and the tetrahedral hydrogen-bonded network is distorted or disrupted by increased coordination found at higher pressures. Consequently, the energy landscape is less partitioned, and molecules rotate more freely. Under these conditions the applied electric field cannot align the water dipoles as easily unless the frequency of the field is low. Therefore, the relaxation times are large. In other words, in

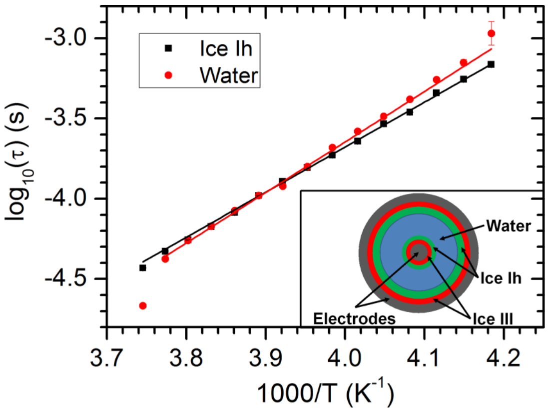

FIG. 3. (Color online) Dielectric relaxation times as a function of inverse temperature for water (red circles) and ice Ih (black squares). The inset shows the cross section of the capacitor with water surrounded by thin shells of ice Ih and ice III.

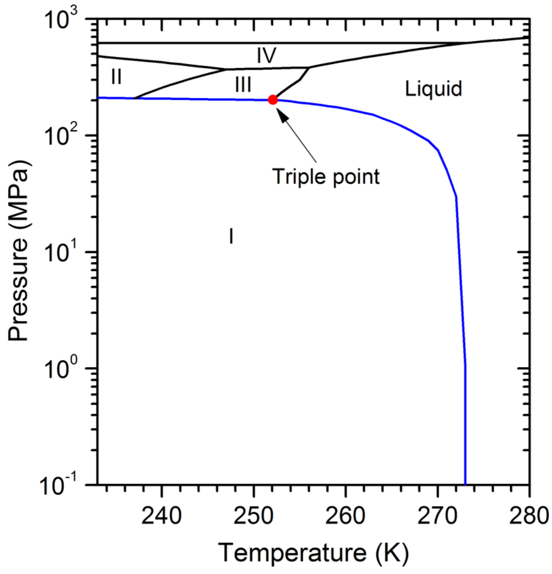

FIG. 4. (Color online) A section of the phase diagram of water in the temperature-pressure range used in this work [5].

ice Ih the dynamics of the dipoles is very slow; in water under pressure the dipoles are abnormally free (because the rotational diffusion increased [38]). It is fascinating to find that their relaxation times are similar. Likewise, the activation energies are similar too: 3.97×10^{-20} J for ice Ih and 4.54×10^{-20} J for the water–ice Ih–ice III sample.

We now go back to the response obtained at 267 K in Fig. 1. As we previously mentioned, the high pressure increases the molecular rotation. This event requires that at least two hydrogen bonds break [40]. Coincidentally, such reorganization of the hydrogen bonds propel the Grotthuss mechanism, which is related to the fast transport of protons [41]. Although authoritative voices claim that the Grotthuss mechanism needs a revision [42], the accepted picture behind this mechanism is that structural diffusion in water takes place. Such diffusion is promoted by the local topology of the H-bond network and couples to the fluxions of the proton wires, specifically collective compressions [43]. Thus, we believe the high values of ϵ' are due to an electrode polarization caused by fast ions that are able to respond to and accumulate at frequencies higher than 10^3 Hz. If our conjecture is correct, the isotherm at 267 K in Fig. 1 tells us that the topology of the network for the Grotthuss mechanism to occur, in pure water, is rather unique. A little bit outside these conditions (267 K and around 100 MPa) the electrode polarization decays as usual.

IV. CONCLUSIONS

Overall, we found a subtle but clear signal of ice III formed when water is cooled below its melting point in a constrained macroscopic volume. With it, we believe ice Ih also formed. We must emphasize that this water–ice III–ice Ih coexistence occurs at complete equilibrium, in contrast to the metastable state of supercooled water, normally studied in capillaries and porous materials. For example, in vermiculite clay (a hydrophilic material), a shift of the main relaxation peak has been found when the temperature decreases [20]. However, in such a study, the shift is only seen when two water layers are confined between the clay platelets (14.96 Å apart). The authors also observed that around 24% of the sample crystallizes at 235 K and the remaining water stays in a supercooled state. In another work, water in white bread (which displays ideal hosting properties to explore nanoconfinement) shows similar shifts at low temperatures [25].

We show that the inner pressure shifts the α peak of normal water to low frequencies (kHz). Finally, we found an intriguing dielectric signal at 267 K, probably caused by fast ionic transport. Our results may have important implications in the understanding of water dynamics under pressure in a macroscopic confinement.

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