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Hidden Slow Dynamics in Water

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It is well known that the structural and dynamical properties of water are of central importance for life on our planet. However, despite this knowledge its structural and dynamical properties are still far from fully understood. In this Letter we show for the first time that water exhibits an anomalously slow relaxation process, which is about 4 orders of magnitude slower than the viscosity-related structural main relaxation. This slow Debye-like process has previously only been observed in monoalcohols and more recently also in polyalcohols, and due to its slowness it is generally believed to be caused by some kind of collective motion of hydrogen-bonded structures. The new finding has important structural and dynamical implications for water.

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Water is one of the most common substances on Earth, and exhibits many unique properties necessary for living organisms. Except for the excellent solvation properties of small polar and ionic compounds due to its polarity and high dielectric constant [1], it has unique hydration properties, which, for instance, play a crucial role in folding, function and stability of proteins, formation of cell membranes, and in reaction and transport processes on which life is dependent [1]. Many of these unique properties, among others, are due to the extensive hydrogen-bonded network between adjacent water molecules [1].

A water molecule can participate in four hydrogen bonds and for a long time the accepted picture has been that the molecules tend to form a tetrahedral hydrogen-bonded structure [2], although the hydrogen bonds have very short lifetimes, which is in the order of 1 ps at room temperature. Recently, however, this picture was questioned, and it has instead been proposed that tetrahedral-like structures are only present in form of clusters, surrounded by more hydrogen-bond distorted structures [3]. Thus, the structure of bulk water is still not fully established, and therefore, still a matter of discussion. Because of the difficulties to directly determining the structure of water we believe that valuable structural insights can be gained from more detailed studies of the dynamics of water.

Normally, glass-forming materials exhibit one main structural α relaxation that is directly coupled to the viscosity and the glass transition of the system, and one or several secondary relaxation processes that are of more local character, the so-called β relaxations [4,5]. In general, the temperature behavior of β relaxations is well described by the Arrhenius law, whereas the slower and more global α relaxation usually shows a Vogel-Fulcher-Tammann (VFT) temperature dependence, $\tau = \tau_0 \exp(DT_0/(T - T_0))$, where D is a parameter that determines the deviation from Arrhenius behavior and τ_0 is the relaxation time when the temperature T goes to infinity. The glass transition temperature T_g of a material corresponds to the temperature where the relaxation time τ of the α relaxation reaches ≈ 100 s.

In addition to the commonly observed α and β relaxations, many hydrogen-bonded liquids, such as monoalcohols [6,7], and more recently polyalcohols [8], display an additional slower relaxation process of Debye character. The origin of this process that has only been observed in hydrogen-bonded liquids is not clear, and therefore, many suggestions have been made that all include some kind of hydrogen-bonded structures [9–12]. The question is if this slow Debye-like relaxation is a universal characteristic for all hydrogen-bonded liquids, including water, and not only a feature of mono- and polyalcohols as previously shown. In fact, based on careful rheological studies such a slow relaxation process has been predicted to be present in all polymers and glass-forming liquids [13].

Glycerol is one of the polyols that recently was shown to exhibit also this Debye-like relaxation [8], and since it previously has been revealed that the Debye-peak is a general phenomenon in mixtures if the individual components or liquids show this feature [14], we have, by use of dielectric spectroscopy, investigated water and mixtures of water and glycerol of different water content. In this letter we show that, indeed, also water exhibits such a low-frequency dielectric Debye peak. The reason for why it has not previously been observed is that it is normally hidden by the large contribution of conductivity and/or electrode polarization that is present at low frequencies in a standard dielectric measurement on liquid water.

The dielectric measurements were performed on a broadband dielectric spectrometer from Novocontrol in the frequency range (10^{-2}–10^{7} Hz). The sample thickness was 0.1 mm in all measurements. The imaginary part of the dielectric response, $\varepsilon^*(f) = \varepsilon'(f) - \varepsilon''(f)$ was analyzed by use of the Cole-Cole function [15] [Eq. (1)] for the Debye peak, and the more general fit function [16] [Eq. (2)]

for the α relaxation

$$\varepsilon''(\omega) = \mathrm{Im}\left(\frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau_{\mathrm{CC}})^\alpha}\right), \tag{1}$$

$$\varepsilon''(\omega) = \frac{\varepsilon''_p}{\frac{(1-C)}{a+b}[b(\omega/\omega_p)^{-a} + a(\omega/\omega_p)^b] + C}, \tag{2}$$

where $\omega = 2\pi f$ is the angular frequency. Specific parameters for the equations are in Eq. (1) the relaxation time τ, the static dielectric constant and the limiting value of the dielectric constant at high frequencies ε_s and ε_∞ respectively, and α is the shape parameter that determines the symmetric broadening of the relaxation peak. In Eq. (2) ω_p and ε''_p are the position and the height of the peak. The parameters a and b are shape parameters that describe the slope of the peak at low and high frequency side, respectively, and the C parameter is a parameter that describes the broadening of the relaxation peak without changing the power laws at high and low-frequency sides.

In this study the conductivity and polarization effects were suppressed by covering one of the electrodes with a thin Teflon film (5 μm), since this type of set up has been shown to reduce such effects [17,18], even if care has to be taken when analyzing the data [19]. To ensure that the observed Debye peak was not caused by the Teflon film we also measured the samples without using the Teflon film and studied the derivative of the real part of the permittivity, which also gave evidence for a weak relaxation process at about the same frequency, as shown in Fig. 1(a).

The slowest and strongest peak shown in Fig. 1(b) was not observed in the measurements where no Teflon film was used and therefore it is most likely due to Maxwell-Wagner interfacial polarization, which is a common feature when charges are blocked at inner boundaries [4]. The high amplitude and Debye shape of the peak further support this interpretation. The origin of the second slowest relaxation is not known and further investigations are needed to clarify its underlying dynamics, and therefore, we will not discuss this process further. The focus in this letter will be on the fastest, and second strongest, relaxation process that is of Debye type, i.e., a process of similar shape to what previously has been observed in mono- and polyalcohols. However, in the case of polyalcohols [8], and in the here investigated mixtures of glycerol with water, this process is hardly seen if no Teflon film is used [see Fig. 1(a), where it is observed in the derivative of the real part (ε') of the permittivity], in contrast to the monoalcohols where the Debye-like process dominates the spectrum. The temperature behavior of the Debye-like process is shown in Fig. 2 for water, glycerol and mixtures of them. As evident from this figure, at the highest temperatures, which is the most interesting region since none of the samples then contain ice (which is the case for water concentrations above the critical concentration ≈ 35 wt % at low temperatures [20,21]) this Debye-like relaxation is slowest in case of pure glycerol, and becomes increasingly faster with increasing water content. Also obvious is that this process follows a non-Arrhenius temperature dependence, in agreement with previous findings for monoalcohols [11].

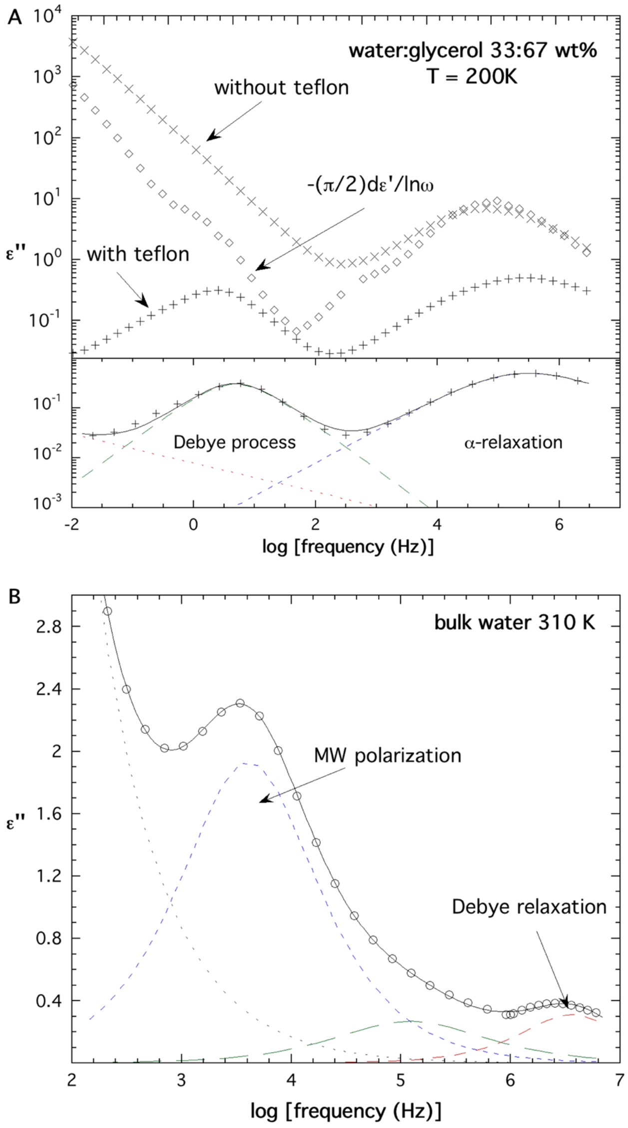

FIG. 1 (color online). Imaginary part (ε'') of the dielectric spectra for (a) a sample with 33 wt % water and 67 wt % glycerol at the temperature 200 K and (b) bulk water at the temperature 310 K. In (a) the sample has been measured both with and without a 5 μm thick Teflon film between the sample and one of the electrodes, and for the measurement without the Teflon film also the derivative of the real part (ε') [25] of the dielectric spectra is shown for comparison. In the lower panel of (a) and in (b) the curve fitting is shown to visualize how the relaxation times of the different relaxation processes were extracted from the measured data. Equation (1) was used for the Debye-like process and the two slower processes shown in (b), and Eq. (2) for the α relaxation, whereas the low-frequency dispersion was fitted by a conductivity term ω^{-1}.

In Fig. 3(a) the temperature dependences of the Debye-like relaxation and the corresponding α relaxation are compared for ice-free samples below the critical water concentration (≈ 35 wt % water). From this figure it is

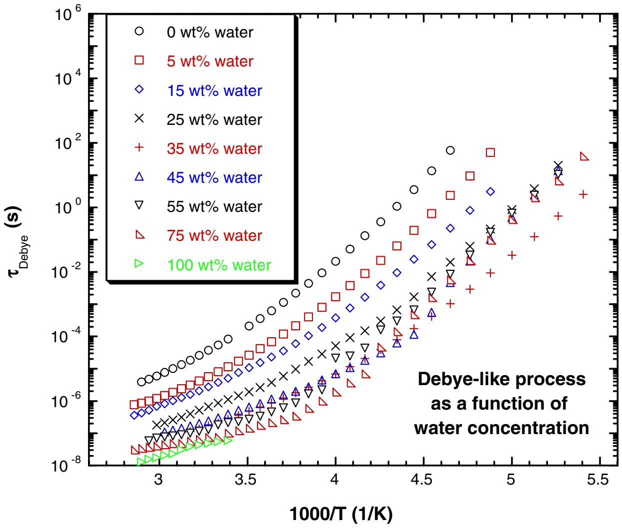

FIG. 2 (color online). The temperature dependence of the Debye-like relaxation process for some of the measured mixtures of different water concentrations ranging from pure glycerol to pure water. The relaxation time τ_{Debye} is plotted as a function of the inverse temperature $(1000/T)$.

seen that both the Debye-process and the α relaxation are well described by a VFT temperature behavior, and that the extrapolated τ_0 must be much larger for the Debye-like process than for the α relaxation. In case of the α relaxation $\tau_{0\alpha}$ is found to be in the region of 10^{-14}–10^{-15} s, which is a relaxation time that corresponds to the quasi-lattice or molecular vibrations that normally is observed for bulk materials. For the Debye-like process, on the other hand, a significant characteristic [22] of monoalcohols is that the relaxation time of this process is several orders of magnitude slower than that of the α relaxation at higher temperatures. In general τ_0 of the Debye-like process approaches a value of 10^{-11} s when the temperature goes to infinity [22], which also is the value found for all samples, including bulk water, in this study. The relatively large value of τ_0 compared to the typical time for vibrations of single molecules suggests that this process is due to some kind of collective motion of larger structural units.

From studies on monoalcohols it has been shown [14] that the temperature dependence of the relaxation time of the Debye-like process is parallel to that of the α relaxation, and the corresponding viscosity of the system. Therefore, in order to find out if there is such a correlation between the structural α relaxation and the process of Debye-type in the here investigated mixtures, we show in Fig. 3(b) a double logarithmic plot of τ_{Debye} vs τ_α. From this plot it is obvious that for the glycerol-rich mixtures the two processes are linearly related to each other (as indicated by a slope $= 1$ in the plot), although the Debye-like process is about 5 orders of magnitude slower than the α relaxation in the measured temperature range. Thus, the behavior of the Debye-like process seems to be the same for the glycerol-rich mixtures as for the monoalcohols.

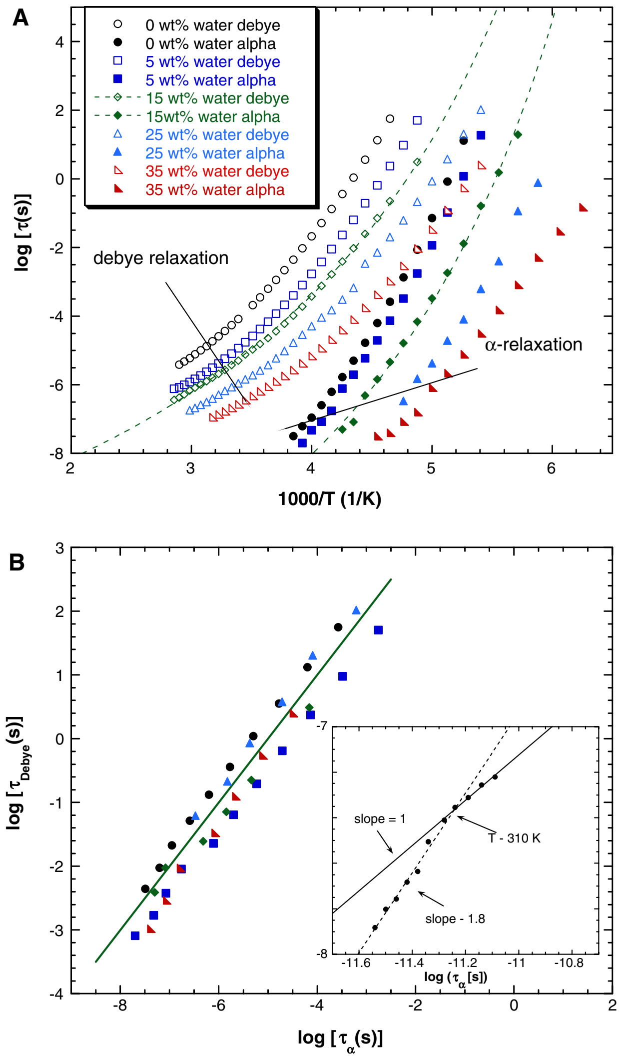

FIG. 3 (color online). (a) The temperature dependences of the Debye-like process and the α relaxation for samples below the critical water concentration, i.e., samples containing such low concentrations of water that they do not form any ice. The dotted lines show the fits to the VFT function for the Debye-like process and the α relaxation occurring in the sample containing 15 wt % water. (b) The relaxation time of the Debye-like process plotted as function of the relaxation time for the α relaxation [symbols as in (a)]. The solid line shows $\tau_{\mathrm{Debye}} = 10^5 \tau_\alpha$, which gives a slope of one in the log-log plot, and clarifies that the two processes are parallel in (a) in the measured temperature range and that the Debye-like process is approximately 10^5 times slower than the α relaxation. The inset in (b) shows the same plot for pure water, where the relaxation times for the α process are taken from Ref. [26]. From this figure it is clear that the linear relation (solid line) between τ_{Debye} and τ_α is only valid at temperatures below 310 K, where $\tau_{\mathrm{Debye}} \approx 10^4 \tau_\alpha$. At higher temperatures the data points are best described by the dashed line, which has a slope of about 1.8 in the log-log plot.

However, in the case of pure water the inset in Fig. 3(b) indicates that this linear relation between τ_{Debye} and τ_α is lost at temperatures above approximately 310 K. The reason for this is most likely that the structural units (discussed below) that are responsible for the slow Debye-like relaxation starts to break up into smaller units at this temperature, leading to a decreasing ratio between τ_{Debye} and τ_{α}. A similar crossover in the relation between τ_{Debye} and τ_{α} is therefore expected to occur also for the water-glycerol mixtures at higher temperatures than the 255 K we have been able to follow the α relaxation to. Note also that the crossover for water occurs at our body temperature, which means that it might have important biological implications. The observation should, however, be considered as a qualitative finding, since the Debye-like process starts to move out of our experimental frequency window at about 320 K. For a more accurate determination of the relaxation times at higher temperatures measurements at higher frequencies are needed.

Interestingly, a low-frequency relaxation process similar to the here observed Debye-like process has recently been predicted from rheology measurements to be a general phenomenon of polymers and glass-forming liquids [13]. The measurements have shown that liquid samples of a sub-mm size exhibit a solid behavior due to long-range interactions that also are expected to give rise to the here observed large time-scale relaxation, as well as other nonlinear phenomena that are unpredictable in the frame of the conventional viscoelastic approach [13]. Thus, if Noirez *et al.* [13] are right, a similar low-frequency relaxation process should be present in all glass-forming materials.

From a structural and dynamical point of view the observed low-frequency relaxation is expected to be associated with some type of structural and/or dynamical inhomogeneity on a length-scale corresponding to the time-scale of the relaxation process. Since the time scale of the Debye-like process is roughly a factor 10^5 slower than the structural α relaxation, which occurs on an approximate length-scale of 1 nm far above the glass transition temperature, the length-scale of the Debye-like relaxation should be of the order 0.1 mm (assuming that the relaxation time is proportional to the size of the moving "particle", in accordance with the Stokes-Einstein relation), which is in perfect agreement with the prediction made by Noirez *et al.* [13].

Whether the Debye-like slow relaxation can be explained by the recently proposed structural model by Huang *et al.* [3] is difficult to establish since they observed structural inhomogeneities on a considerably shorter length-scale than expected from the frequency of the Debye-like process. A possibility is, however, that the distorted hydrogen-bonded structures are connected to chainlike structures with slow dynamics similar to the so-called normal mode of polymers [23]. If such a polymer-like dynamics is responsible for the slow Debye-like process and can be described by the Rouse theory [24] the relaxation time should correspond to a length-scale of the chain structures of about 100 nm.

To conclude, we show that the well-known Debye-like slow relaxation in monoalcohols is considerably more general than previously thought, by proving its existence also in water, glycerol and mixtures of them. The new finding has important structural and dynamical implications for water and indicates that water exhibits structural and/or dynamical inhomogeneities on considerably longer length scales than previously thought.

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