Glass Transition and Relaxation Processes in Supercooled Water

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(Received 5 May 2004; published 8 December 2004)

Many of water's peculiar physical properties are still not well understood, and one of the most important unresolved questions is its glass transition related dynamics. The consensus has been to accept a glass transition temperature (T_g) around 136 K, but this value has been questioned and reassigned to about 165 K. We find evidence that the dielectric relaxation process of confined water that has been associated with the long accepted T_g of water (130–140 K) must be a local process which is not related to the actual glass transition. Rather, our data indicate a glass transition at 160–165 K for bulk water and about 175 K for confined water (depending on the confining system).

DOI: 10.1103/PhysRevLett.93.245702 PACS numbers: 64.70.Pf, 77.22.Gm, 87.15.–v

The glass transition and its related dynamics are important unresolved issues in condensed matter physics [1]. The main feature of the glass transition is the slowing down of the main (α) relaxation process when the temperature is lowered towards the liquid-glass transition temperature T_g. In addition to the dominant α relaxation, a secondary relaxation, commonly referred to as the Johari-Goldstein or β relaxation, often exists at higher frequencies [2]. In contrast to the α relaxation, the β relaxation is a local process [3] which normally follows an Arrhenius temperature dependence.

The study of glass transition related properties of water has attracted the interest of researchers in a wide range of research fields. In contrast to simple liquids, there is a dispute linking the behavior of water at a low degree of supercooling to that of glassy water found below T_g, typically believed to be 136 K [4–6]. Attempts have been done to connect the thermodynamic behavior of water [7–11] in the temperature range between the glassy state and the homogenous nucleation temperature (235 K). In this temperature range, water appears to be a strong liquid (Arrhenius temperature dependence), while in the temperature region above $T = 235$ K water is a very fragile liquid (non-Arrhenius temperature dependence). Based on the above-mentioned observations, Angell and co-workers proposed that T_g of water might be in the range 160–180 K [12–15].

Confining water geometrically is a way to avoid crystallization and entering the experimentally inaccessible region for bulk water (150–235 K). We therefore chose to study supercooled water confined in vermiculite clay [16] and in white bread. Bread is a complex system mainly composed of polysaccharides (~50%, of which starch is the major component), proteins (~8%, principally gluten), and water (~40%) [17], whereas vermiculite clay has a two-dimensional structure consisting of parallel clay platelets with intercalating adsorbed water and Na^+ ions in between platelets [18]. Both systems are able to adsorb water in well-defined amounts. Totally dry Na-vermiculite clays were obtained by drying at 423 K in a vacuum oven for 48 h. After the drying, we carefully weighed the clay pieces, and they were thereafter submerged in distilled water for 2 days to obtain full hydration. The bread samples were obtained by first drying white bread for 7 days under vacuum at 348 K and thereafter by hydration to the desired water content (<1, 4, 6, 10, and 17 wt%, respectively). The actual state of water in food polymers is less known. Previous studies on the hydration of bread and its main components [19–22] have shown that water is distributed unequally by both components (starch and gluten) while a fraction of water remains in the free state. This free water is unfreezable as the temperature decreased below the freezing point as measured by differential scanning calorimetry (DSC) and was found to be partly mobile [20,22]. The high capability to absorb water without any crystallization makes bread an ideal hosting system to study confined glassy water.

To study the dynamics of water confined in these systems, we performed broadband dielectric spectroscopy (Novocontrol Alpha, 10^{-2}–10^7 Hz). Details of the procedure are given in Ref. [23]. In the low hydration bread samples (<10 wt%), there is no evidence of ice formation when the samples are cooled from room temperature down to 93 K as measured by differential scanning calorimetry and only 3% of the water confined in vermiculite clay crystallizes at 235 K. Therefore we are able to study confined water in these systems in the supercooled liquid state. Spectra for both systems are shown in insets 1 and 2 of Fig. 1(a).

For the bread sample with low hydration level (<1 wt%), we observed a very broad relaxation entering in the experimental frequency window at around 135 K. Between 140 and 300 K, the relaxation peak is symmetric and can be described by the empirical Cole-Cole equation. The lines in inset 1 of Fig. 1(a) represent least-square fits to a superposition of a power law, proportional to f^{-n}, where $n \approx 0.4$, and the imaginary part of a Cole-Cole (CC) function: $\varepsilon^*(f) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)[1 + (i2\pi f\tau)^\alpha]^{-1}$. Here ε_s and ε_∞ are the static and high frequency limiting values of the dielectric constant, respectively, α is the width parameter, and τ is the relaxation time.

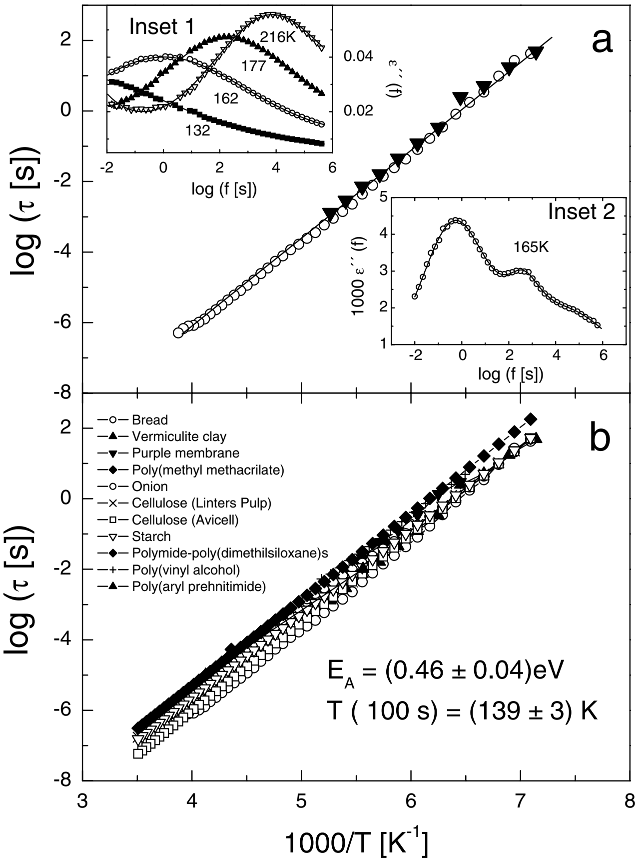

FIG. 1. (a) Temperature dependence of the relaxation times obtained from fits of the spectra from confined water in vermiculite clay (solid triangles) and bread (open circles). The solid line represents the Arrhenius equation, $\tau = \tau_0 \exp(E_A/kT)$. The activation energy (E_A) for this process is found to be $E_A = 0.48$ and 0.50 eV for water in bread and vermiculite clay, respectively. The relaxation time at 100 s is 136 and 138 K for confined water in the two systems, while τ_0, the extrapolation at infinite temperature, is 10^{-16} s for both systems. (b) Temperature dependence of the relaxation times for water confined in a wide variety of systems. In this figure open symbols represent water confined in biological materials, whereas solid symbols represent water confined in mineral and synthetic systems. Biological systems: cellulose avicell (0.2 wt %) [24], Merck starch (0.2 wt %) [24], lyocell filaments (0.2 wt %) [24], onion (7.8 wt %) [25], purple membrane [26], and bread (this work). Mineral and synthetic systems: Polyimide-poly(dimethylsiloxane) hybrid networks [27], Poly(aryl prehnitimide) [28], poly(methyl methacrylate) [29], Poly(vinyl alcohol) hydrogel (10 wt %) and confined water in vermiculite clay (this work). It is important to note that the biological (i.e., soft) samples in this figure contain small quantities of water (usually less than 1 wt %). These small quantities give rise to the local relaxation observed in the dielectric response. Inset 1: Frequency dependence of the imaginary part $\varepsilon''(f)$ of the dielectric relaxation $\varepsilon^*(f)$ of the confined water in bread at some representative temperatures. Inset 2: $\varepsilon''(f)$ of the two H_2O layer clay system at 165 K. Three processes can be identified at this temperature. The process at low frequency is the main process whose relaxation times are plotted in the Arrhenius plot.

Three processes can be identified at low temperatures in the dielectric spectrum of the two H_2O layer clay [23], as shown in inset 2 in Fig. 1(a). The two small processes at higher frequency were related to crystalline water since they also appear on a reference sample of ice [16]. The main peak at low frequencies can also be fitted with a Cole-Cole function with an almost temperature independent relaxation strength and width.

Evidently both systems present the same relaxation time for the main process, as shown in Fig. 1(a). Is this a mere coincidence? Figure 1(b) shows the relaxation times for confined water in several systems [24–29], whose constituent components are diverse in nature but all are hydrated with water, which does not crystallize upon cooling, or the crystallization is very low. Astonishingly, the dynamic response in these systems is almost independent of the nature of the confinement. Thus, this implies that perturbations of the environment do not substantially affect this relaxation (as long as the water concentration is low enough to prevent possible influences from other water promoted relaxation processes in soft materials). The average activation energy calculated from Fig. 1(b) is $E_A = (0.46 \pm 0.04)$ eV and the extrapolation of the temperature at 100 s $T = (139 \pm 3)$ K.

Certainly, complex interactions between water molecules and supporting materials are established and a strong distortion of the hydrogen bond network is likely to take place. This implies that a cooperative relaxation process, such as the α relaxation, should be strongly affected or even hindered by the widely different environments (generally, the relaxation dynamics of confined water shows a retardation due to interactions with the confining host materials [30]). Since no such substantial environmental dependency can be observed for this process, this indicates that we are not observing the cooperative α relaxation as previously thought. Moreover, calorimetric data show no glass transition in the range 130–140 K. Instead, a more probable explanation is that we observe a local β-like process of water molecules interacting with the host material. Indeed, broad symmetric peaks with Arrhenius temperature dependence are spectral characteristics typical of β processes. This interpretation agrees with the conclusions first drawn from extrapolations of the β relaxation in polypropylene glycol (PPG) oligomers [31].

If this relaxation process is not the α relaxation, the long accepted T_g of water (130–140 K) [4–6] is dubious. This T_g value is to a large extent based on extrapolations of T_g values for mixtures of water and some other molecule, e.g., a salt [32]. In these systems, however, the hydrogen bonded network of water molecules is easily destroyed such that the T_g of the mixture should be increasingly determined by the above discussed local β-like relaxation process as the water concentration increases. Thus, an extrapolation to 100% water will, in network breaking systems, reflect the local relaxation process and give a "T_g" at 130–140 K, where this process reaches a relaxation time of $\approx$ 100 s; see Fig. 1. As the α relaxation is a cooperative process, more reliable extrapolations should thus be based on mixtures with waterlike properties when it comes to the hydrogen bonding capacity. We therefore performed DSC on water mixed with H-[OCH(CH$_3$)CH$_2$]$_n$-OH, with $n = 1, 2$, and 3 (note that $n = 0$ is water), which expand the network rather than breaking it. Indeed, extrapolations of T_g for these systems give a higher T_g value ($\approx$162 K), as shown in Fig. 2. This T_g is close to the new T_g suggested by Velikov *et al.* [12] and Yue and Angell [13]. Interestingly, DSC of bread with intermediate hydration levels (4, 6, and 10 wt %) reveals a clear endothermic transition around 170 K, while it is absent at lower or higher hydration levels. It thus seems a delicate balance in the hydration level is necessary to observe the α relaxation of confined water. At low hydration levels (or in small cavities such as in the case of fully hydrated vermiculite clay), only the β-like relaxation is revealed. At intermediate hydration levels, water clusters are large enough to show cooperative relaxation via the α process, but the level is still too low to allow any crystallization. Finally, at high hydration levels, crystallization inhibits cooperative motions and again only local motions are produced.

Figure 3 shows the dielectric spectra at 183 K of bread with a water content of 10 wt %. The signal is markedly different in comparison with the sample of the lowest water content [see inset 1 in Fig. 1(a)]. In this case, the main peak has a relaxation time of 100 s at 176 K, i.e., at about the same temperature as the calorimetric glass transition (see inset 1 in Fig. 3). Since the calorimetric T_g was observed only for intermediate water contents, this strongly suggests that the observed dielectric main process in this case corresponds to the α relaxation of water.

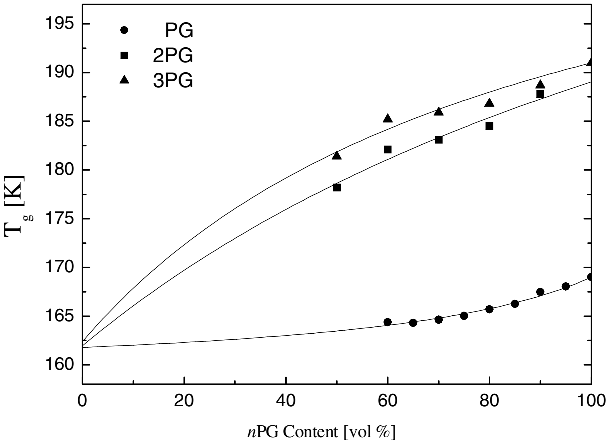

FIG. 2. Calorimetric T_g versus nPG (propylene glycol) content for aqueous mixtures H-[OCH(CH$_3$)CH$_2$]$_n$-OH, with $n = 1, 2$, and 3. The solid lines represent the best fit of the experimental data to the Gordon-Taylor equation [37], $T_g(x) = [T_{g1}x + T_{g2}k(1 - x)]/[x + k(1 - x)]$, where T_{g1} and T_{g2} are the nPG and water glass transition temperatures, respectively, x is the nPG content, and k a nonlinear parameter. The fitting procedure was done by fixing T_{g1} to nPG glass transition temperature (except for 2PG whose T_g is anomalously high) and leaving T_{g2} and k as free parameters. A value of 162.1 ± 0.3 K for the water's glass transition was obtained. Although the extrapolation is based on high nPG concentration (crystallization occurs for water contents higher than 50 wt %), the extrapolation for the three mixtures is very consistent.

Based on the discussion above, we used a superposition of two functions representing the α and β relaxations. To describe the data at each temperature we used a Cole-Cole equation for the β process with the same relaxation time and shape parameter as for the sample with low water content. We are thus assuming that the β relaxation is a local process which does not change with increasing water content. For the α relaxation peak, we used an empirical equation which is a good frequency domain representation of the Kohlrausch-Williams-Watts equation [33],

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

where ε''_p is the amplitude at the peak maximum, ω_p is

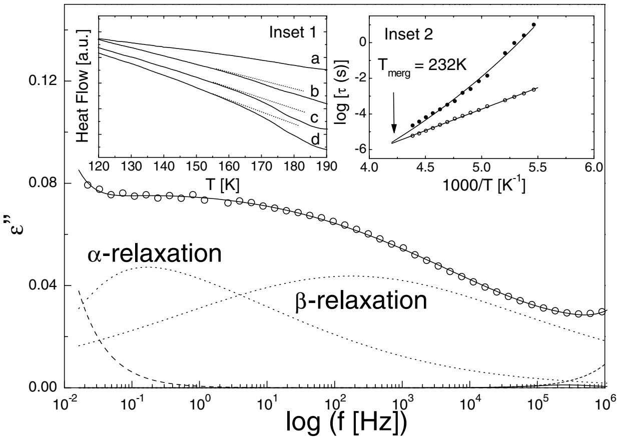

FIG. 3. The dielectric loss ε'' for confined water at 10% hydration level. The solid line represents the least-square fit to a superposition of a power law, the imaginary part of a CC function (for the β relaxation), and Eq. (1). Inset 1: Water glass transition at ~173 ± 3 K, as seen in the DSC scans independently of the hydration level (curves b–d). Curves a–d were obtained after quenching the sample in liquid nitrogen, annealing at 160 K for 90 min to accentuate the effect, cooling to 110 K, and finally heating at a rate of 30 K/min. Curves a–d are from a bread sample containing increasing amounts of water: <1 (a), 4 (b), 6 (c), and 10 wt % (d). The same sample was used for all curves. Note that curve a shows no detectable glass transition because, for the lowest hydration level, there is not enough water to observe the cooperative α relaxation. Inset 2: Temperature dependences of the relaxation times obtained from fits of the dielectric spectra of confined water in bread. The open symbols denote the β relaxation, whereas the solid symbols show the α relaxation time of the water.

the peak frequency, and b is the shape parameter (for the α relaxation). In the fitting procedure these three parameters were free. Thus, the solid line in Fig. 3 represents the least-square fit to a superposition of a power law, the imaginary part of a CC function (for the β relaxation) and Eq. (1). Additionally, a very small second CC function can be detected at higher frequencies (this peak is due to some crystallization in the sample and could not be observed above 200 K). The α process for water has an almost temperature independent shape parameter, b ($b \approx 0.3$).

Inset 2 in Fig. 3 shows the obtained relaxation times for the α and β processes. The temperature dependence of the slowest process can be analyzed with a Vogel-Fulcher-Tammann equation, $\tau = \tau_0 \exp[DT_0/(T - T_0)]$, giving $\tau_0 = 10^{-15}$ s, $T_0 = 103$ K, and $D = 28.5$. From D, a value of the fragility parameter $m = 40$ is obtained (m is the slope of the $\log\tau$ versus T_g/T curve at T_g). This value suggests that deeply supercooled water is a relatively strong glass former in contrast to moderately supercooled bulk water. It is also intriguing to note that the obtained α and β relaxations times merge at a temperature ($T = 232$ K) not far from the temperature for which several quantities diverge when their high temperature behavior is fitted with a power law ($T_S = 228$ K) [34].

The scenario outlined in this Letter for bread at a 9 wt% hydration level merits further studies of other systems. Materials such as cellulose, starch [35], and PPG-water solutions [36] show a similar behavior at high water contents. Thus, it seems as other systems show a similar α relaxation as examined here. However, as mentioned above, every system needs a systematic and extensive study to determine the hydration level for which it may be possible to observe both contributions (the local β-like process and the α relaxation).

To summarize, the main relaxation process observed in many water containing systems is not the cooperative α relaxation of water but due to a local β-like process. Hence, the findings are consistent with a T_g of water at a higher temperature ($\approx$160–165 K) than commonly believed as suggested by Velikov *et al.* [12] and Yue and Angell [13]. The results have important implications in biology, e.g., for the understanding of glass-transition-like effects observed in the same temperature range for hydrated proteins.

S. C. is grateful to the CONICET for support. J. S. is supported by a grant from the Knut and Alice Wallenberg Foundation. Financial support to J. S. from the Swedish Foundation for Strategic Research is gratefully acknowledged

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