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Dielectric Studies Deny Existence of Ultraviscous Fragile Water

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The glass transition, a relaxation phenomenon, sets the low temperature limit to the liquid state. Glassy water that forms only under extreme quenching conditions is unstable against crystallization. Opinions differ on whether the glass transition can be observed at all. Here we measure the dielectric tanδ for easily glassforming waterlike aqueous solutions, H_2O-H_2O_2 and H_2O-N_2H_4, to characterize the behavior of such systems during passage through their glass transitions. All show unambiguous T_g values of 136–140 K, the value generally assigned to pure water. However, the behavior of $\varepsilon''/\varepsilon'$ is quite different from that in amorphous water in the same temperature range. Our findings eliminate "ultraviscous fragile liquid" as a possible description of water between 136 K and crystallization, but leave "ultraviscous stong liquid" a possibility to be considered.

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The most abundant state of water in the Universe is presumed to be the amorphous state because this is the form in which water exists in the vastness of interstellar space, as thin films on dust particles [1–3]. Together with the evidence that a relatively immobile form of water occurs on many biological surfaces [4], this highlights the importance of the amorphous solid states of water. There are at least two distinct forms [5,6], possibly more [7,8], and the relation between terminal annealing states within a single configuration space megabasin, on the one hand, and distinct polyamorphic forms, occupying distinct megabasins [9] on the other, is still being worked out [3,10]. We will refer to low density and high density forms as LDA and HDA without considering the variations such as Very HDA [7,8] observable within each.

A recent review devoted to amorphous water [3] shows that amorphous water is in an unusually high state of order. Its entropy is closer to that of the crystal than in any other glass, and its phonons exhibit crystal-like lifetimes at low temperatures. The order is particularly evident within the LDA form, which is also notable [11] for lacking the usual two level systems previously considered ubiquitous in the glassy state [12]. Glassy water, it is argued [3], is close to the ideal glass state which, by definition, has no configurational entropy, and hence is a "third law substance." The irony of this situation is that the glass transition temperature for this nearly "ideal" glass is a matter of dispute, the resolution of which is the object of this Letter.

Very many aqueous solutions are strongly glassforming, and their glass transition temperatures are easily assigned from the unusually large jumps in heat capacity they manifest at T_g. The solution data, which in some cases contain as little as 3 mol % of second component, all suggest, by short extrapolation, that glassy water should show a comparable doubling of its heat capacity at a temperature of 136–140 K [13]. However, differential scanning calorimetry (DSC) scans of relaxed amorphous water through this range show nothing at all unless special annealing procedures are followed [14]. After annealing at the appropriate temperature, an extremely weak increase (1/14th of the expected value) can be observed [14]. This endotherm, which extends over a very wide temperature range has been broadly accepted as the "glass transition of water". Its weakness and its exceptional width (relative to T_g) have remained quite unexplained except for the suggestion that a "fragile-to-strong" liquid state transition may have occurred [15].

The existence of a fragile-to-strong transition, however, is incompatible with a strong body of opinion, based on diffusivity measurements at 145–150 K [16] and other arguments [17], that water is a fragile liquid at these temperatures with T_g expected at 136 K by the Vogel-Fulcher-Tammann equation extrapolations of the diffusivity data. The consistency of this extrapolation with the binary solution T_g extrapolations, and with the calorimetry of Ref. [14], has proven convincing to most commentators on the subject, as summarized in a recent authoritative review [18]. An alternative opinion, namely, that water remains in the glassy state up to crystallization [19–22], evidently [18] awaits validation. What is needed here is a set of reliable measurements of physical relaxation behavior in the range between the putative T_g at 136 K and the crystallization temperature.

The crystallization of amorphous solid water (ASW) has been reported at various temperatures T_C in the range 140–170 K. As might be expected, the T_C value found depends on the sample preparation method, on the one hand, and on the heating rate, on the other. The highest recorded T_C values, 165 K by Olander and Rice [23] and 170 K by Koverda *et al.* [24], were both obtained on films deposited from the dilute vapor phase. Olander and Rice carefully examined the relation between amorphous film properties and the ASW deposition rate, with the object of minimizing the possibility of generating crystallization nuclei during the deposition. Relaxation studies between

136 and 165 K, perhaps 170 K, thus appear feasible for rapid scanning experiments.

The most precise method for studying relaxation in condensed phases at this time is dielectric spectroscopy, which has the exceptional ability to detect very small energy dissipations [25]. Koverda, Bogdanov, and Skripov (KBS) [24] and, more recently, Johari, Hallbrucker, and Mayer (JHM) [26] have applied the method to annealed amorphous water films, and their results, for temperature scanning at a fixed frequency of 1 kHz, are shown in Fig. 1. The data were in each case reported as the ratio of imaginary to real parts of the dielectric susceptibility $\varepsilon''/\varepsilon' = \tan\delta$ since this quantity does not depend on sample dimensions.

Both data sets show comparable temperature-dependent increases in $\tan\delta$ above 136 K, though the actual magnitudes differ. The JHM data (supported by our findings reported below) show that the break at 136 K in the KBS data (and assigned by them to the glass transition) was due to instrumental limitations. The deposit studied by KBS, on the other hand, survived to considerably higher temperatures than those of JHM, before showing a sudden drop to the same value on crystallization.

We now report the behavior of the same quantity, $\tan\delta$, measured on glasses and liquids in three solutions in the system H_2O-N_2H_4 and one solution in the H_2O-H_2O_2 system, using a state-of-the-art dielectric spectrometer [25]. These solutions vitrify during moderately fast cooling and then exhibit strong glass transitions during reheating. T_g is only a weak function of solution composition, falling in the range of 135–140 K [27]. An extrapolation to 100% H_2O would yield a T_g for water somewhat below the familiar 136 K value for the first system and slightly above it for the second (see below).

The behavior of $\tan\delta$ for these solutions, vitrified in the dielectric cell and then scanned at a constant 1 kHz between 120 K and the crystallization temperature at 170 K, is shown in Fig. 2. In contrast to the case of ASW, the entire relaxation spectrum can now be seen. The maximum in $\tan\delta$, observed shortly above the T_g, occurs when the condition $\omega\tau = 1$ is met. Therefore the relaxation time at this temperature may be obtained. Using variable frequency studies (to be reported elsewhere), the relaxation time has been obtained as a function of temperature in the range 140–165 K, over which it varies from 10^{-1}–10^{-5} s. Extrapolation using a Vogel-Fulcher-Tammann equation form allows the temperature at which the relaxation time reaches 100 s, frequently chosen as T_g, to be assessed.

The comparison of T ($\tau_D = 100$ s) with the calorimetric T_g values is shown in Fig. 3, and the expected close agreement is found. Figure 3 includes data for solutions in the system H_2O-H_2O_2 [28]. Only at the composition 33 mol % H_2O_2 was an H_2O-H_2O_2 solution found to be stable enough against crystallization for the $\tan\delta$ vs $\log f$ relation to be followed through the $\tan\delta$ maximum, as in Fig. 2. Again, T_g, based on the $\tau_D = 100$ s criterion, agrees with the calorimetric value. For this system T_g is invariant with composition, at 140 K [27,29].

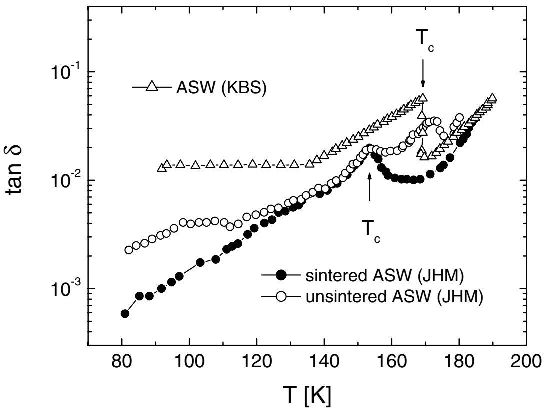

FIG. 1. Dielectric loss tangent $\varepsilon''/\varepsilon'$ vs temperature for amorphous solid water from two laboratories [24,26], showing steady increases in loss up to the crystallization temperature where sudden decreases occurs. The break at ~136 K, attributed to the glass transition by Koverda *et al.* [24], is not reproduced in the study of Johari *et al.* [26], nor is it supported by the present work on related glasses. The high dissipation, at low temperatures, of the "as deposited" film in Ref. [26] is removed by the "sintering" process which also changes the crystallization path.

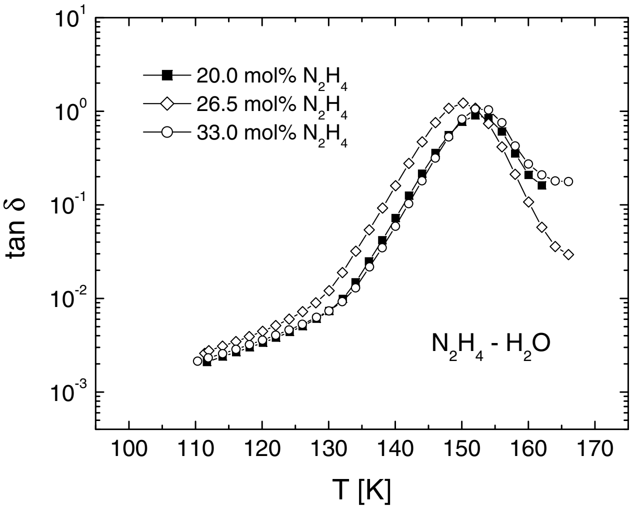

FIG. 2. The loss tangent at fixed frequency (1 kHz) for H_2O-N_2H_4 solutions, as a function of temperature. The peak value allows the temperature at which the relaxation time reaches $(2\pi f)^{-1} = 1.6 \times 10^{-4}$ s to be assessed. Note that the change in slope at ~135 K occurs when the dissipation due to the alpha relaxation rises in strength above the $1/f$ noise level, and is not an indicator of the glass transition. If any one of the frequency, distribution of relaxation times, or fragility were to be different, the slope change would occur at a different temperature [25].

In Fig. 4 we combine the tanδ findings for these four aqueous solutions with the tanδ data for ASW from Fig. 1, including only the "sintered" ASW data of JHM. The implications of Fig. 4 are immediate and obvious. Where all the binary solutions show a major change of slope of the tanδ vs T plot, as T passes through 135–140 K, ASW (though supposedly [14,16–18,24,26] having the same T_g) shows nothing beyond a continuation of the low temperature $1/f$ noise. In view of the very large dielectric constant, any tendency to begin the tanδ upswing should be easy to detect.

The absence of any sign of a maximum in the tanδ data for ASW, to compare with those seen in each one of the solution samples, tells us that there is no temperature in the range 136–165 K in which the relaxation time reaches values of 1.6×10^{-4} s. Evidently, from the absence of even a beginning upswing in the KBS data, τ_D for ASW does not even reach the value of 100 s characteristic of the glass transition in this range. The JHM data, originally presented on a linear scale, show some structure that is much suppressed when using the log scale forced by the wide data range of our study. It is possible that some early stage of relaxation is being manifested in those data. However, in view of the KBS results (Fig. 1), this is more likely a manifestation of instability against crystallization than of glass transition precursor effects.

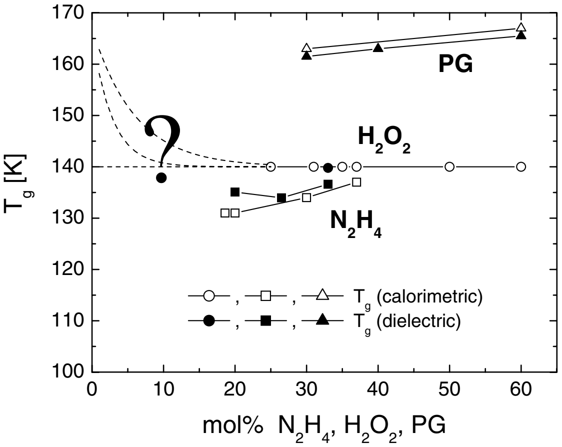

FIG. 3. The variation of T_g with composition in H_2O-N_2H_4 and H_2O-H_2O_2 solutions [19,20,27,29]. Comparison is made of DSC data with the temperatures at which the dielectric relaxation time extrapolates to 100 s, and the expected level of agreement is found. (DSC scans in [27,29] were conducted at the commonly used 10 K/s rather than the 20 K/s needed to give$\tau_H = 100$ s). Data for propylene glycol (PG) + water solutions are included for later discussion. The upswing in T_g for solutions approaching the pure water axis may seem arbitrary and improbable until it is realized that ASW is an open tetrahedral network, and that all open tetrahedral network glasses show similar rapid T_g decreases on addition of second components that disrupt the network.

Since relaxation time relates to the diffusion coefficient D via the Einstein equation in the form $\tau = \lambda^2/6D$, where λ is the wavelength of the principal relaxation mode (obtained from the peak of the structure factor, and of atomic dimensions), and since τ never reaches a value of 100 s, the value of D never rises above 10^{-22} m^2/s in the range of this study. Our findings are thus quite incompatible with the earlier diffusivity measurements in the same temperature range [16]. In other words, either the dielectric data, obtained independently by two groups (Fig. 1), or the diffusivity data responsible for the current belief that "ultraviscous fragile water" exists, must be wrong. The dielectric data are, on the other hand, entirely compatible with our earlier conclusions [21] based on the observation of incomplete enthalpy relaxation before crystallization [28] in hyperquenched glassy water. The simplest conclusion of this analysis is that ASW remains a glass up till crystallization. However, we should recognize a further interesting possibility, as follows.

Let us suppose that 136 K is indeed the glass temperature but that, as suggested in Refs. [15,30], the liquid

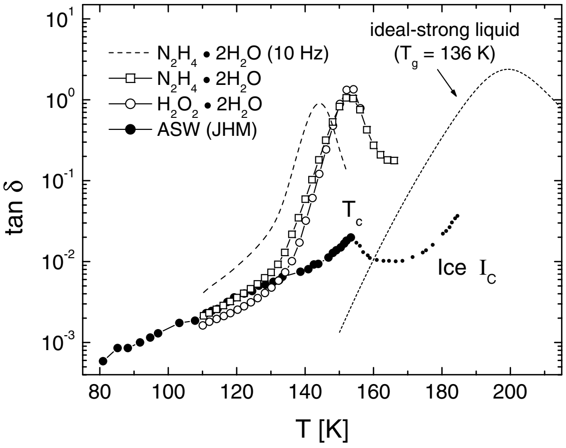

FIG. 4. Comparison of the variation of 1 kHz loss tangents for aqueous N_2H_4 and H_2O_2 solutions of $T_g = 135$–140 K with that of sintered ASW, as reported by JHM [26]. Data for ice Ic after sintered ASW crystallization are included as the dotted line. It is clear that the behavior of ASW is inconsistent with that expected for a material with $T_g \sim 136$ K. Since the ASW data of KBS [24] shown in Fig. 1 extend to high temperatures without showing any upswing, it would appear that T_g for ASW must lie above 160 K, hence be unobservable. However, it is possible that the behavior of ASW could be associated with very strong liquid behavior after a T_g at 136 K. The dashed line shows the expectation for an "ideal strong liquid" (see text) a relaxation, to which the $1/f$ noise must be added. It is unfortunate that neither of the tanδ studies of ASW [24,26] were conducted at a lower frequency, e.g., 10 Hz, because then comparison with our own low frequency data would have resolved the "strong liquid" ambiguity. The low temperature long-dashed curve shows our results for N_2H_4-$2H_2O$ for 10 Hz.

generated at the glass transition is an extremely strong liquid (as would be necessary to understand the "non-existent T_g" in Ref. [20] and the exceptionally small increase of heat capacity observed in the annealing studies of Hallbrucker *et al.* [14]). Let us assume the extreme case in which water has, in addition to T_g of 136 K, exponential relaxation and Arrhenius behavior of the relaxation time with pre-exponent of 1.0×10^{-14} s, i. e., the ideal strong liquid. In this case the isothermal loss spectra will be a series of Debye relaxations with height determined by the value assumed for ϵ_s, e.g., 80. The maximum of the 136 K isotherm will occur at 1 mHz, corresponding to $\tau_D = 100$ s.

From these spectra we construct the tanδ vs T plot shown as a dashed line in Fig. 4. This is a provocative result. We see that, while the data of JHM in Fig. 4 exclude the possibility that water above 136 K is a fragile liquid [16,17], or even a liquid intermediate in character like the present solutions, those data could be accommodated within a strong liquid scenario while maintaining that T_g is 136 K (though the data of KBS which extend to 170 K would have to be rejected). According to Fig. 4, lower frequency data (e.g., 10 Hz instead of 1 kHz) on the dynamics of ASW could provide a more decisive resolution of this "strong liquid" issue.

It should be recalled here that the analysis by Starr *et al.* [31] of thermodynamic data, from studies of supercooled water and amorphous solid water, required that water undergo a fragile-to-strong liquid transition in the range 200–220 K, and that this would cause the glass transition strength to greatly decrease, and presumably also to change form.

Some insight into the actual behavior may be available from the study of water in nanoscopic confinement, when crystallization is more easily avoided. Calorimetric studies have been made of both soft-confined water in hydroxylated methacrylate polymers [32] and hard-confined water in silica [33]. In each case water domains of ~3 nm diameter are believed present. The calorimetric results have features is common, showing continuous increases up to a maximum at 220 K in the first case and 230 K in the second. Both have features in common with the heat capacity behavior deduced in Ref. [32]. The hydrogel sample showed a glass transitionlike onset phenomenon at 162 K consistent with the indications of Fig. 3, in particular, with the data on propylene glycol plus water solutions. The best account of the behavior of water is likely to be some combination of the two scenarios we have outlined [31].

In summary, dielectric studies of glassforming aqueous solutions demonstrate that LDA above 136 K cannot be an ultraviscous fragile liquid. Most likely it is not a liquid at all, but the possibility that it is an ultraviscous strong liquid, following a fragile-to strong transition, cannot be excluded.

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