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Interpretation of the GHz to THz dielectric relaxation dynamics of water in the framework of the Coupling Model

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ABSTRACT

The microscopic origins of the processes in water observed at temperatures above and below room temperature by dielectric relaxation spectroscopy in the range from GHz to beyond THz are identified by three sequential and interrelated contributions in the framework of the Coupling Model. Appearing after vibration and boson peak is the caged water dynamics. Cage decays with the onset of the primitive relaxation of the Coupling Model (CM), which is practically coincident with the nearly exponential structural α-relaxation. These sequential processes explain the nearly Debye α-loss peak, the high frequency power law (HFPL) associated with it, and the higher frequency dispersion before reaching the vibrational contributions. High frequency and short time experimental data of several glass-formers obtained by different techniques are presented to show the same three processes with the same relationship between them, as proposed for water. Crucial supports of the CM explanation come from neutron scattering experiments on water showing that: (1) caging and decaging indeed occurs in the HFPL regime; (2) the dynamics of the HFPL is independent of the scattering vector Q, in accord with the HFPL is comprised of caged dynamics and decaging; and (3) the terminal process is normal diffusion, justifying the 20 GHz dielectric loss peak originates from the structural α-relaxation, which follows after the completion of decaging, i.e. the end of the HFPL regime.

1. Introduction

Lunkenheimer et al. [1] combined dielectric, THz and far-infrared techniques to provide high quality isothermal broadband dielectric spectra of pure water over the frequency range from 100 MHz to 20 THz and at selected temperatures from 275 to 350 K. Their dielectric loss data, $\varepsilon''(\nu)$, reproduced in Fig. 1 offer more detailed information on the high frequencies dynamics than before. The prominent loss peak at room temperature located at about 20 GHz and the faster dynamic processes at high frequencies has been interpreted in different and incompatible ways by various authors in the past [2–12], and at more recent times [1, 13–18]. Remarkably the controversy in the interpretations of the dynamics of water in the high frequency regime of practical importance [1] continues to the present time. These various interpretations have been reviewed and critically discussed by Lunkenheimer et al. [1], and will not be repeated in the present paper. The purpose of the paper is to offer yet another interpretation based on the predictions of the Coupling Model (CM), and the findings from the most recent dielectric relaxation study of Lunkenheimer et al. and the neutron scattering measurements of Arbe et al. [18]. The CM interpretation is also supported by the broadband loss spectra of a water solution with 17.3 mol% LiCl and glycerol considered by Lunkenheimer et al. in their interpretation, as well as depolarized light scattering data of pure water [19], hydration water [20], glycerol [21], and other related systems [22].

2. Interpretation based on caged dynamics as precursor of β and α relaxation

2.1. Dielectric data

The prominent loss peaks of pure water has frequency dependence at the temperatures are relatively well fitted by the Fourier transform of the exponential or Debye relaxation function or by the Cole-Davidson (CD) function [23] as shown in Fig. 1. The origin of the two vertical blue lines added will be explained later. However there is excess loss over the $A\nu^{-1}$ of the Debye fit or the power law $A\nu^{-0.9}$ at 275 K and $A\nu^{-0.95}$ at 350 K of the CD fits. The excess suggests the contribution from some faster dynamic process or processes. Lunkenheimer et al. (L et al.) characterize the excess as a second slightly less steep power law, superimposed to the ν^{-1} decrease of a Debye relaxation and refer to it as the high-frequency power law (HFPL). Currently the 20 GHz Debye or CD loss peak has been interpreted by others principally in two ways.

Following earlier ideas, Hansen et al. [17] identified this 20 GHz loss peak to be the Debye relaxation originating from the dynamics of

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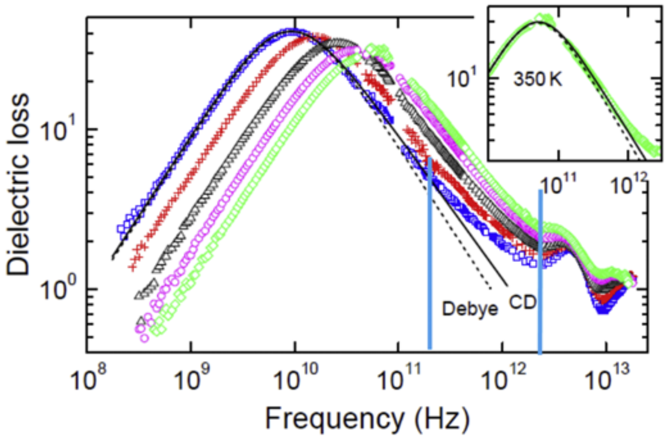

Fig. 1. Dielectric loss spectra of water at selected temperatures at 275, 290, 310, 330 and 350 K. The dashed and solid lines are fits with the Debye and Cole-Davidson functions, respectively. Inset: Loss for 350 K with fits. See text for the origin of the two blue lines drawn in relation to neutron scattering results. Figure is taken from Lunkenheimer et al. [1] and reproduced by permission of APS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

clusters formed by hydrogen-bonded molecules like that found in monohydroxy alcohols [24–27]. Faster than this Debye relaxation is the α-relaxation, which is considerably less intense and contribute to the excess on the high frequency flank of the Debye process. However, based on the temperature dependence of the spectral features, L et al. found their data contradict the interpretation of Hansen et al. As pointed out by L et al., at low temperatures in the alcohols the alpha relaxation often becomes more separated from the Debye peak and, thus, becomes better visible in the spectra [27]. This is not the case in water and the water:LiCl solution [1], where only the main peak and an excess wing (HFPL) is seen even at the lowest temperatures [1]. The 20 GHz peak of water is also present in the LiCl solutions, and it becomes much broader than Debye at low temperatures, in contrast to the behavior of the Debye relaxation in the alcohols. The same behavior can be found in the dielectric relaxation in aqueous solutions of hydrazine and hydrogen peroxide [28]. The data from the neutron scattering experiment [18] also are at odds with the interpretation of Hansen et al. notably that the terminal relaxation having the characteristic Q^{-2}-dependence for its relaxation time is diffusive. But this is accord with interpretation of the dielectric loss peak by L et al. as the structural or the primary α-relaxation of water governing the fluidity, and the wing-like excess contribution (HFPL) is due to the contribution of a boson peak on the high frequency flank of the α-relaxation.

We agree with L et al. on interpreting the 20 GHz dielectric loss peak of water as the structural α-relaxation of water, and believe that their interpretation of the HFPL can be close to the truth. Notwithstanding, since final solution of the problem is open, we give our own interpretation of the faster dynamics including the HFPL, which is different from L et al. and others. The idea behind our interpretation is based on the general rule of the time evolution of dynamics of glass-forming liquids from the Coupling Model [29–32]. In the course of time, after the vibrations including the Boson peak (if present), but before the onset of the primary and secondary relaxation process with characteristic relaxation times τ_α and τ_β respectively, molecules (or atoms) are caged. In the caged molecules regime, the susceptibility is manifested by a power law $B\nu^{-c}$ with a small positive power $c \gg 1$. Such small c values justifies the term, nearly constant loss (NCL), for the susceptibility of the caged dynamics The NCL corresponds to the flat valleys of the dielectric loss spectra seen at higher temperatures in glycerol and propylene glycol, and suggested by interpolation in the 17.3 mol% water:LiCl solution in Fig. 3 of L et al. The NCL of caged dynamics persists till the cage decays by the onset of the primitive relaxation of the CM and development of the Johari-Goldstein (JG) β-relaxation at lower frequencies. The combination of cage decay and the onset of the primitive relaxation contribute to the HFPL of water in the GHz-THz dielectric data of L et al. Water distinguishes from the other glass-formers in not only limited in study to this high frequency region but also having narrow α-relaxation close to that of Debye. Therefore in water the primitive relaxation as well as the JG β-relaxation are practically indistinguishable from the α-relaxation. The other glass-formers and 17.3 mol% water:LiCl solution can be studied down to low frequencies and the JG β-relaxation can be observed as an excess over the fit to the α-loss peak by either the Cole-Davidson function or the Fourier transform of the Kohlrausch-Williams-Watts (KWW) function,

$$\varphi(t) = \exp\left[-\left(\frac{t}{\tau_\alpha}\right)^{1-n}\right], 0 \le n < 1 \qquad (1)$$

if the JG β-relaxation is not resolved [32, 33]. In Eq. 1, τ_α is the structural α-relaxation time, and n is the coupling parameter of the CM. At frequencies higher than this excess wing, is the contribution from the cage decay together with the primitive relaxation, and still at higher frequencies is the NCL of the caged dynamics. If the JG β-relaxation is resolved usually its relaxation time is comparable to that of the primitive relaxation. For these glass-formers, supports of the cage dynamics is coupled to the primitive relaxation or the JG β-relaxation [29-34] come from the change of temperature dependence of the either the NCL measured by terahertz spectroscopy or the mean square displacement measured by neutron scattering at the secondary glass transition temperature $T_{g\beta}$ [35–37].

At high temperatures and high frequencies such as in the study of L et al., the range of frequencies where the caged dynamics can be discerned in the susceptibility is drastically reduced. It is limited by the vibration and Boson peak contribution at high frequencies, and the JG β-relaxation at lower frequencies. Whether the caged dynamics contribution in terms of the NCL can be detected unambiguously or not, its existence is not in doubt because it is a universal and necessary feature of the dynamics before the onset of relaxation according to the Coupling Model. Besides it is also the main ingredient in the idealized mode coupling theory (MCT) [38], although our treatment of caged dynamics is not related to MCT. To enhance credibility of our thesis of the presence of the caged dynamics as precursor of the α-relaxation in pure water and 17.3 mol% water:LiCl solution, we cite below some direct evidence of it in other glass-forming materials in the frequency range (GHz–THz), or the equivalent time range (0.1–100 ps) comparable to that in Fig. 1.

Broadband dielectric loss data of 17.3 mol% water:LiCl solution was given by L et al. to show similarity in the spectral features of water and water:LiCl solutions. Previously it was shown that the NCL exists in water solutions of 26.5 mol% N_2H_4 as well as 22.5 mol% ethylene glycol at low temperatures and frequencies [39]. In these aqueous mixtures, the NCL was detected at loss level below that presented by L et al. of the ε″ data of water solution of 17.3 mol% LiCl. This suggests that the NCL of water:LiCl solutions maintain its presence in the GHz to THz region. The appearance of the NCL associated with caged dynamics at low frequencies in glycerol for temperatures 184 K and below in Fig. 3b of L et al. is unquestionable as can be seen from the observed frequency dependence of $\varepsilon''=B\nu^{-c}$ with $c \approx 0.1$ or small. The subsequent rise of ε'' with decreasing ν with another power law (excess wing) is due to the combination of cage decay and the onset of the primitive relaxation of the Coupling Model (CM) and the development of the JG β-relaxation [29–34]. On increasing temperatures of glycerol from 223 to 363 K in Fig. 3b, the NCL frequency region (flat valley) becomes narrower, and eventually is changed to a shallow minimum due to the additive vibrational contribution on the high frequency side and the high-frequency power law (HFPL) on the low frequency side of the α-loss peak. The spectra at 323, 363 and 413 K of glycerol for frequencies