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RESEARCH ARTICLE

Does exist an anomalous sound dispersion in supercooled water?

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Acoustic sound velocity of water in the supercooled regime shows a peculiar behaviour. Accordingly to the available data, sound velocity displays a complex behaviour below −15 °C, here anomalous frequency dispersion phenomena seem to appear and need to be understood. In particular lower frequencies data at a few tens of KHz show leveling-off of the sound velocity value below -25 °C, with a possible minimum around -30 °C. Other data at higher frequencies, around 1 GHz, in comparison with the low frequency data, could instead suggest the existence of a "negative dispersion", yet other high frequency data show a normal dispersion behaviour. To get new insight into this topic, we made measurements of acoustic sound velocity in bulk water in the liquid and supercooled phase down to -29 °C by means of a heterodyne detected transient grating (TG) experiment at an unexplored frequency value around 100 MHz.

Keywords: supercooled water; sound velocities; transient grating; 78.47.+p; 78.40.Dw; 61.20.Ne; 61.20.Lc; 43.30.Es; 43.35.Bf;

1. Introduction

Despite the paramount interest of water, many physic properties of this liquid remain to be clarified [1]. In particular, several thermodynamic and dynamic features exhibit an anomalous dependence on temperature in the water supercooled phase [1–6]. Since the discover of these anomalies, the liquid matter community is puzzling about the nature and origin of these water unexpected phenomena. Different physic models has been introduced in order to describe the complex water scenario [6], nevertheless many relevant questions are still open and further research investigations are required [7]. In the liquid and supercooled water also the acoustic phenomena show peculiar and specific behaviours. These have been discussed in many research papers, for a review see [7, 8]. Considering only the low wave-vector/frequency range ($q < 50\ \mu^{-1}$ and $\nu < 10$ GHz), the main striking effect is the steep decrease with decreasing temperatures of the adiabatic sound velocity [9], opposite to the normal liquid trend. For $T > -15$ °C, this decrease does not display any dispersion phenomena (i.e. its temperature slope is independent from the sound wave-vector/frequency). Below this temperature, accordingly to the available data, the sound displays a complex behaviour where the dispersion phenomena need to be clarified [7]. In particular the lower frequency measurements (54 KHz) [10–12] show a quite surprising phenomena: a leveling-off of the sound velocity below -25 °C, with a possible minimum around -30 °C. A comparison of

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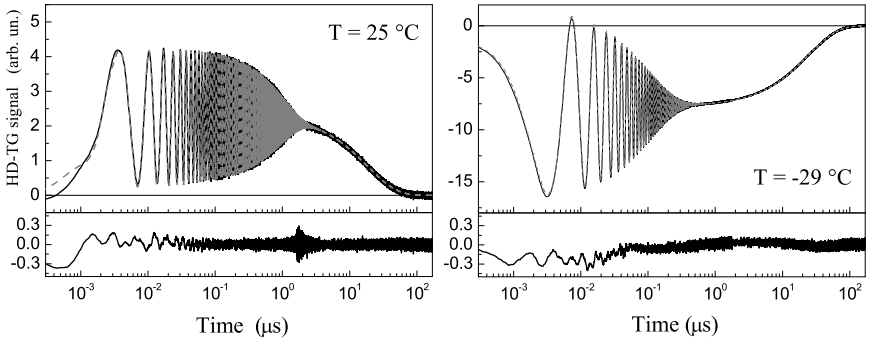

Figure 1. HD-TG data on water at $q = 0.630\ \mu m^{-1}$ at two different temperatures. The data show acoustic oscillations and slow thermal exponential decay. Comparison between data and fit (dashed line) is also reported. The fit is hardly visible, so we report also the residuals obtained by the difference between data and fit in an amplified scale.

these data with sound velocities obtained at higher frequencies ($\geq$ 900 MHz) [13–18], produces an even more confused scenario that could suggest the existence of a "negative dispersion" (sound velocity would decrease with increasing frequency) in the water supercooled phase [7, 9, 13, 16]. We performed a transient grating (TG) experiment on the supercooled phase of bulk water down to -29 °C, extending the previous investigation [9] for more then 10 degrees in the supercooled phase. The TG experiment enables us to measure the sound velocity of water in a frequency range (100 MHz) previously unexplored and particular meaningful in order to clarify the summarized complex scenario.

2. Experiments and data

The experimental details has been described in previous paper [9], here we recall the main characteristics. In a transient grating experiment with heterodyne detection (HD-TG) two infrared laser pulses interfere within the sample to produce a spatial modulation of the dielectric constant. The relaxation of the induced transient modulation is probed by the Bragg scattering of a third laser beam, typically of different wavelength. The diffracted beam is then beaten with a local field in order to obtain the heterodyne detection. In the HD-TG experiment used here, the infrared pump pulses had a 1064 nm wavelength, a temporal length of 20 ps and repetition rate of 10 Hz (Nd-YAG EKSPLA PL2143). The typically used pump pulse energy was 5 mJ. The probing beam, instead, was a continuous-wave laser at 532 nm produced by a diode-pumped intracavity-doubled Nd-YVO (Verdi-Coherent). The heterodyne signal was detected by a fast avalanche photodiode with a bandwidth of 1 GHz (APD, Hamamatsu) and amplified with a DC-800 MHz AVTECH amplifier. After that it was recorded by a digital oscilloscope with a bandwidth of 7 GHz at a sampling rate of 20 Gs/s (Tektronix TDS7704B). We performed the measurements on sealed vial of cylindrical shape, prepared for pharmaceutical purposes by Angelini company, that allows to reach a temperature of -29 °C. In the experimental set-up, the sample temperature is controlled by a home-made cryostat with a stability of 0.1 °C. The vial is inserted into an aluminium holder fixed to the cold plate of a Peltier cooler; the temperature is controlled by a platinum thermo-resistance in thermal contact with the aluminium holder. The HD-TG measure the material response function that according to the hydrodynamic models can be connected to the density time evolution [9, 19]. In this specific case, the measured signal can be

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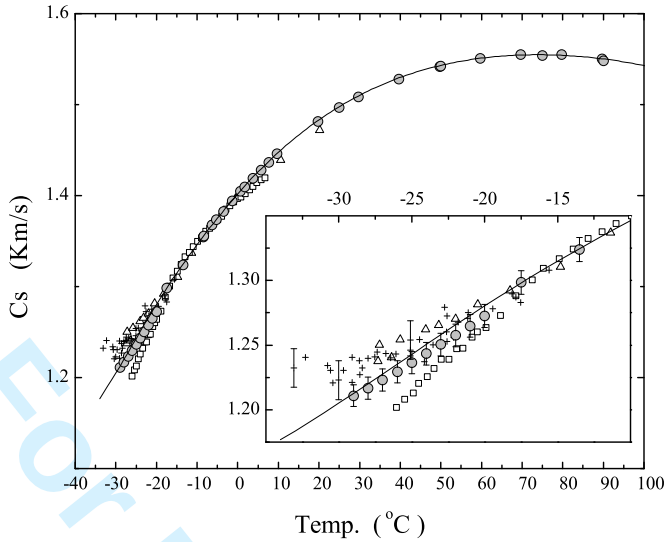

Figure 2. Temperature dependence of the water sound velocity. Our data (•) are compared with other measurements. Ultrasonic data: at 54 KHz (+) from Ref. [12], at 925 MHz (□) from Ref.[20]. Light scattering data: at 1.27 GHz (△) from Ref.[17]. In the inset we report a magnification of the low temperature data, where the unexpected dispersion effect for ultrasonic data clearly appears. The continuous line correspond to the hydrodynamic adiabatic sound velocities calculated using the thermodynamic values.

cast in the following form:

$$S^{HD-TG}(q,t) \propto \; Ae^{-\Gamma t}cos[\omega(q)t] + \; Be^{-\Gamma t}sin[\omega(q)t] + Ce^{-\Gamma_T t} \qquad (1)$$

where ω, Γ are the sound frequency and damping rate and Γ_T the thermal damping rate. The full definition of the hydrodynamic model and the fitting procedure is reported in ref. [9]. The signal definition, reported in eq.1, enables a very good fit of the HD-TG data, see fig.1. Performing the fit of all TG data we obtained the temperature dependence of the water sound velocities, see fig.2. In particular we report the measurement of the water sound velocity for $q = 0.63\ \mu\text{m}^{-1}$, corresponding to a frequency of about $f = \omega/2\pi \simeq 140$ MHz. Our data show a very good agreement with all reported data confirming that there is no dispersion effects in the liquid and weakly supercooled water, over ≈ -15 °C. Indeed the sound velocity data from literature in the supercooled region below -15 °C are quite misleading. In fact, the very low frequency data (~ 50 KHz) [12] are in very good agreement with the light scattering data [17] corresponding to a much higher frequency (~ 1 GHz), furthermore this data show a flattening versus the low temperature. Vice versa other ultrasonic data [20] characterized by an intermediate frequency (~ 900 MHz) show a clear departure. Our data (~ 100 MHz) report sound velocities below the light scattering data (~ 1 GHz) (△ in figure 2), as expected for normal sound dispersion, but surely over the ~ 900 MHz data (□ in figure). The sound velocities from our TG data are compatible within the error bars with the ~ 50 KHz data (+ in figure), but they show a much weaker bending of the slope.

3. Discussion

The positive dispersion that is observed in the light scattering measurement of C_s at relatively high-frequencies (around 1-10 GHz) must be addressed to dynamic

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processes [17, 18]. The increase of sound velocity with increasing frequency is due to the viscoelastic processes connected with structural relaxation time. The expected structural relaxation times, for the lower temperatures analysed, is of the order of about ten picoseconds [21] corresponding to a factor $\tau\omega \sim 0.1$ for a frequency of 5 GHz. This value is small but not negligible in order to consider the sound velocity totally hydrodynamic. The same argument can not be applied to understand the lower frequencies sound velocities data that should be interpreted by purely thermodynamic model. In fact the hydrodynamic sound velocity is completely defined by the thermodynamic parameters, being $C_0 = \sqrt{\frac{1}{\rho K_T}\frac{c_p}{c_v}}$, where ρ is the mass density, K_T is the isothermal compressibility, c_p and c_v are the isobaric and isochoric specific heats, respectively [7]. The 50 KHz sound data have been compared with a calculation of C_0 reporting a minimum around of it around -25 C. We repeated such calculation using more recent thermodynamic data and the relation $c_v = c_p - vT\frac{\alpha^2}{K_T}$, being α the thermal expansivity. The utilized thermodynamic data ρ and α are from [22], K_T and c_p from [23]. As it is clear from figure 2 our data are in very good agreement with the thermodynamic calculation of C_0. This is proving that the low frequency ($\sim$ 100 MHz) sound velocities in supercooled water does show a purely thermodynamic nature and its temperature dependence is correctly defined by the combination of well known anomalies present in the thermodynamic parameters. According to our data the leveling-off of the sound velocity is doubtful. If it exist, it is surely much weaker that reported in the previous works [10–12]. Moreover, the ultrasonic data ($\sim$ 900 MHz) [13] seems affected by some experimental drawback that produces a systematic reduction of the velocities. So trying to give an answer to the question stated in the title, does not exist a negative dispersion phenomena in the supercooled water and the sound starts to display a positive dispersion, due to the structural relaxation processes, for frequencies $\geq$ 1 GHz.

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