Pressure Evolution of the High-Frequency Sound Velocity in Liquid Water

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The high-frequency sound velocity v_∞ of liquid water has been determined to densities of 1.37 g/cm^3 by inelastic x-ray scattering. In comparison to the hydrodynamic sound velocity v_0, the increase of v_∞ with density is substantially less pronounced, indicating that, at high density, the hydrogen-bond network is decreasingly relevant to the physical properties of liquid water. Furthermore, we observe an anomaly in v_∞ at densities around 1.12 g/cm^3, contrasting the smooth density evolution of v_0.

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Despite the importance of water in natural science and its unique role in defining biological activity, the structural and dynamical properties of liquid water are far from being completely understood. Numerous experimental and theoretical studies [1,2] have already been devoted to understanding the distinctive properties of water and, in particular, the role of the intermolecular hydrogen bonds. There is a common agreement that the unique physicochemical behavior of water arises from the hydrogen-bond organization of water molecules, which is characterized by an open three-dimensional hydrogen-bond network with an almost perfect tetrahedral arrangement of nearest neighbors. Three models are currently proposed to explain the properties and anomalies of water: (i) the existence of a liquid-liquid transition line between two liquid phases of different densities [3,4], (ii) a singularity-free scenario in which the thermodynamic anomalies are related to the presence of low-density and low-entropy structural heterogeneities [5], and (iii) a description within the framework of mode-coupling theory, initially developed to describe the properties of glass-forming liquids [6]. It remains, however, a challenge to find discriminating experimental tests. Most of the work on water has been focused on the changes of its properties with temperature, but to a lesser extent on its properties under pressure. Early pressure studies dealt with the evolution of thermodynamic and transport properties such as density, heat capacity, compressibility, longitudinal relaxation time, diffusion coefficient, and zero-frequency sound velocity [2,7–9]. More recent pressure work focused on the microscopic structural changes of the liquid water structure: neutron and x-ray scattering experiments were performed to pressures of 1.6 [10–12] and 0.8 GPa [13], respectively.

Previous inelastic x-ray and neutron scattering (IXS and INS) work focused to a large extent on the temperature evolution of the high-frequency dynamics at ambient pressure [14–18]. These experiments revealed a particularly large dispersion effect in the sound velocity as a function of frequency, which—at variance with many other liquids [19]—takes place at very high frequencies, i.e., in the terahertz region. Specifically, at $T = 277$ K and ambient pressure, the dispersion of the longitudinal sound velocity has been found to bring v from its hydrodynamic value, $v_0 = 1500$ m/s to $v_\infty = 3000$ m/s, i.e., an increase of a factor of 2. This transition from the hydrodynamic, or zero-frequency, to the infinite-frequency sound regime is directly observed at room temperature for the excitation with wave vector $Q_t = 2$ nm^{-1} and energy $E_t = \hbar\Omega(Q_t) = 3$ meV. It was soon realized that this transition is qualitatively similar to the sound velocity dispersion in glass-forming liquids, due to a structural relaxation process, dubbed α process. If τ is the characteristic time of this relaxation process, the system has a solidlike elastic behavior for $\Omega(Q)\tau \gg 1$ and a viscous one for $\Omega(Q)\tau \ll 1$ [16,17]. In the case of liquid water, the derived values of τ are in the picosecond time scale. They roughly follow an Arrhenius behavior with an activation energy comparable to the hydrogen-bond energy. This has clarified that, in water, the α process is associated with the rearrangement of molecular structures kept together by the hydrogen bond. On a time scale short with respect to the lifetime of these H-bonded local structures the collective dynamics is very similar to that of the solid state, i.e., ice [15]. In the opposite limit, the dynamics is strongly coupled with the making and breaking of the hydrogen-bond network [16]. The difference between v_0 and v_∞ is directly related to the strength of the relaxation, and therefore, in this picture, the determination of v_∞ provides a handle on a parameter sensitive to the microscopic dynamical and structural properties of the liquid, and its comparison to v_0 provides a sensible method to monitor the relevance of the hydrogen bonding.

In this Letter, we present inelastic x-ray scattering results on the infinite-frequency limit of the sound velocity, v_∞, in liquid water to pressures of 2.7 GPa. Comparison with results on the zero-frequency sound velocity, v_0,

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reveals a significantly weaker pressure dependence of v_∞. More specifically, the ratio v_∞/v_0 decreases from 2.1 at ambient pressure to 1.2 at 2.7 GPa, a typical value observed in simple liquids such as lithium, cesium, and argon [20–22]. Based on the interpretation of previous IXS experiments [15–17] our results indicate the decreasing role of the hydrogen-bond network in the high-frequency dynamics of water, and the evolution of water from an associated to a simple liquid. Moreover, we observe an anomaly in the density dependence of v_∞ at densities around $\rho = 1.12\ \mathrm{g/cm^3}$, which is absent in the density evolution of v_0. This result emphasizes the importance of this density domain, which encompasses the region where the water-ice system displays characteristic changes and properties.

The experiment was performed on beam line ID28 at the European Synchrotron Radiation Facility. A detailed description of the instrument can be found elsewhere [23–25]. We utilized the silicon (11 11 11) and silicon (9 9 9) configurations, giving total instrumental energy resolutions of 1.6 and 3.0 meV full-width-half-maximum (FWHM), respectively. The momentum transfer, $Q = 2k_0 \sin(\theta_s/2)$, where k_0 is the wave vector of the incident photons and θ_s the scattering angle, was selected by rotating the analyzer arm in the horizontal plane. The transverse dimensions of the focused x-ray beam were 0.25 horizontal $\times$ 0.06 vertical mm^2 (FWHM). The Q resolution was set to $0.4\ \mathrm{nm}^{-1}$. Energy scans, performed by varying the monochromator temperature with respect to that of the analyzer crystals, took about 150 min, and each Q point was obtained by averaging four [Si(11 11 11)] or five [Si(9 9 9)] scans. The data were normalized to the intensity of the incident beam. The liquid sample was studied as a function of density by changing pressure. To this purpose two distinctly different samples set-ups were utilized. A Large Volume Cell (LVC), containing $\approx 1\ \mathrm{cm}^3$ sample volume, provided data from ambient pressure up to $P = 0.38$ GPa. Experiments were performed at 277 K and the pressure (determined from a calibrated strain gauge) and temperature stability were better than ± 0.0005 GPa at 0.2 GPa and ± 1 K. The large sample size allowed to perform the experiment with an energy resolution of 1.6 meV FWHM. A Diamond Anvil Cell (DAC), containing $10^{-5}\ \mathrm{cm}^3$ sample volume, was utilized between 0.32 and 2.7 GPa. Data from 0.32 to 1.4 GPa were taken at $T = 297$ K, while data above 1.4 GPa were taken at 410 K to avoid crystallization. The pressure was determined by the ruby luminescence technique; the temperature was measured close to the sample by a thermocouple. The accuracy of pressure and temperature measurements in the DAC were better than ± 0.05 GPa ($\pm$ 0.1 GPa for the data points at 410 K) and ± 1 K. The small sample size required to perform the experiment with the Si(9 9 9) configuration, where a higher incident photon flux is available. For both LVC and DAC setup data points were taken in the 3–9 nm^{-1} Q-transfer range at $\Delta Q = 1\ \mathrm{nm}^{-1}$ intervals in order to construct a reliable dispersion relation.

Examples of IXS spectra as a function of Q are reported in Figs. 1(a) and 1(b) for two selected pressure values obtained, respectively, using the LVC and the DAC. The spectra are analyzed using a model function composed of the sum of a Lorentzian and of a damped harmonic oscillator (DHO) model. The Lorentzian line accounts for the quasielastic contribution and the DHO for the two side peaks, whose energy position is $E(Q)$. This model function was convoluted with the experimentally determined resolution function and fitted to the IXS data utilizing a standard χ^2-minimization routine. The total fits to the data are also shown in Figs. 1, together with their two individual contributions. The energy dispersion of the inelastic signal with Q is shown in the respective insets. The value of v_∞ is obtained from the slope of a linear fit to the dispersion relation. All fits were performed in the same 3 to 9 nm^{-1} interval to avoid the Q region where the effects of the α relaxation are expected [16,17].

The density dependence of v_∞ is reported in Fig. 2. For each P, T point we calculated the density using the liquid water equation of state (EOS) [26]. We observe a very weak temperature dependence between 277 and 410 K, and therefore the density evolution of v_∞, although measured at different temperatures, can be considered to represent an isothermal evolution. This high-frequency limit of the sound velocity is compared to the sound velocity in the zero-frequency limit v_0, as measured by Brillouin light scattering [7,8] and ultrasound techniques [9]. These data

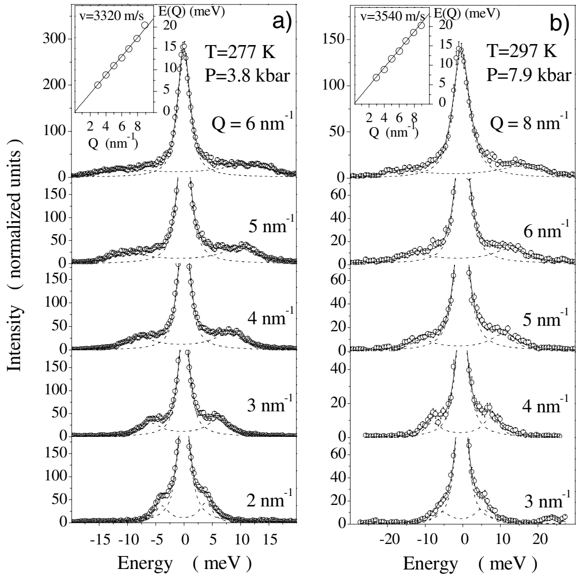

FIG. 1. Selected examples of IXS spectra of liquid water (circles) taken at the indicated Q values in the LVC (a) and in the DAC (b) at the indicated pressures and temperatures. The data are shown together with the total fits and their individual components, as explained in the text. The insets report the dispersion relation obtained for these two P, T points and the linear fits from which the indicated values of v are derived.

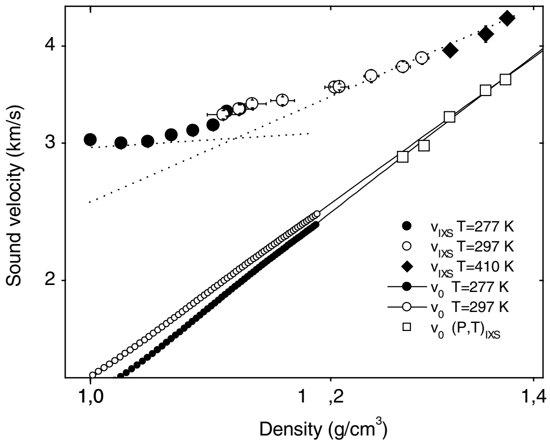

FIG. 2. Density dependence of v_∞ as derived from data sets as those shown in Fig. 1 on a logarithmic scale: LVC (full circles), DAC (open circles and full diamonds). The density evolution of v_0 at 277 and 297 K was obtained from the water equation of state [26]. The solid lines show their extrapolation to higher densities where water would freeze. The squares indicate the value of v_0 at the P, T points of the IXS experiment. The two dotted lines, intersecting at $\rho \approx 1.1$ g/cm^3, emphasize the different low and high-density behaviors of v_∞.

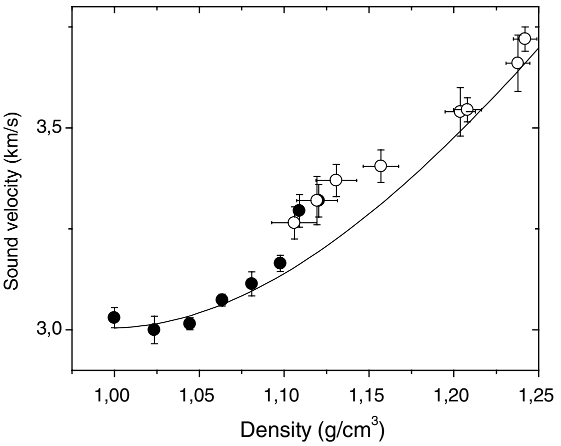

FIG. 3. Anomalous behavior of v_∞ around the density value of 1.12 g/cm^3. The solid line is a third order polynomial fit to v_∞ using the low and high-density points outside the anomalous region. LVC (full circles), DAC (open circles).

are consistent with the values of v_0 obtained from the water EOS [26], which are shown for $T = 277$ K (small filled circles) and 297 K (small open circles). A linear extrapolation (solid lines), on a logarithmic scale, of these two $v_0(\rho)$ data sets to densities where water would crystallize, yields a good agreement with the calculated values of v_0 for the P, T points of the IXS experiment, thus testifying that the T dependence of v_0 becomes less and less relevant with increasing density.

We observe a distinctly different evolution of v_∞ and v_0. v_∞ has a weaker density dependence than v_0, and consequently the two sound velocities approach each other as density increases. The difference between v_∞ and v_0, which is associated with the strength of the coupling between the density fluctuations and the structural rearrangements controlled by the hydrogen bond, is therefore strongly reduced in water with increasing density. This implies that the structural relaxation process is less capable of affecting the density fluctuations spectrum. Consequently, the relevance of the H-bond network tends to disappear, and the behavior of liquid water becomes that of a normal liquid. This interpretation is further supported by inspecting the ratio v_∞/v_0, which almost monotonically decreases from a value of 2.1 at $\rho = 1.0$ g/cm^3 down to 1.2 at $\rho = 1.37$ g/cm^3. While the unusually high value of 2.1 at ambient pressure constitutes one of the main anomalies of the liquid water high-frequency dynamics, its high-density value of 1.2 is comparable to the one observed in simple liquids such as lithium, cesium, and argon [20–22]. Our conclusions validate the trend of hydrogen-bond breaking inferred from an experimental structural study [12] up to 0.4 GPa (1.126 g/cm^3) and from recent molecular dynamics simulations [27–29]. These studies indicate a strong modification of the local liquid structure, i.e., the transition from an open, hydrogen bonded tetrahedral structure, to a high-density form with nontetrahedral oxygen angles and a collapsed second coordination shell.

Furthermore, Fig. 2 reveals another feature in the density region around 1.12 g/cm^3. Contrary to the smooth behavior of v_0, v_∞ shows a clear bump. This is highlighted in Fig. 3 which shows an enlargement of the low-density region. We introduced a polynomial fit to represent the smooth part of the density evolution of v_∞ by a fit of the data at low and high density, excluding the anomalous region. This is justified considering that the high-density data can be truly considered isothermal, and the bump observed is visible beyond any error bar by each data set. The observation of an anomaly in v_∞ suggests that, in contrast to the smoothness of the density evolution of *macroscopic* parameters such as v_0, there are *microscopic* structural rearrangement processes, affecting the hydrogen-bond network in this considered density region. We further note that this anomaly is located in a density region where (i) both the shear viscosity [30] and the melting curve of water display a minimum, (ii) a second critical point of water is predicted in molecular dynamics simulations [31,32] or derived from the discontinuity of the ice IV melting line [4], and (iii) the stability regions of low-density and high-density amorphous ice are separated. Consequently, the present observation tends to demonstrate that the anomalies in the macroscopic quantities in the density region around $\rho = 1.12$ g/cm^3 could be related to an anomaly in the terahertz dynamics of liquid water. Further experiments and molecular dynamics simulations are needed to firmly assess the origin and the role of the anomalous behavior of v_∞.

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