Structural Relaxation in Liquid Water by Inelastic UV Scattering

C. Masciovecchio,[1] S. C. Santucci,[1,2] A. Gessini,[1] S. Di Fonzo,[1] G. Ruocco,[3] and F. Sette[4]
[1]*Sincrotrone Trieste, S.S. 14 km 163, 5 in Area Science Park, 34012 Basovizza Trieste, Italy*
[2]*Dipartimento di Fisica, Università di Perugia, Via Pascoli 1, 06100 Perugia, Italy*
[3]*Dipartimento di Fisica and INFM, Università di Roma "La Sapienza", P. A. Moro 2, 00185 Roma, Italy*
[4]*European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble, France*
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Using the novel synchrotron radiation based inelastic ultraviolet scattering technique, the dynamic structure factor of normal and supercooled liquid water has been measured at a momentum transfer $Q \approx 0.1$ nm^{-1}, in the temperature range 260–340 K. The structural (α) relaxation has been observed in the supercooled temperature region ($T \leq 273$ K), where the inverse relaxation time matches the frequency of the probed sound modes. The T dependence of the relaxation time shows a diverging behavior with a critical temperature $T \approx 220$ K. These results provide a unique experimental opportunity to frame the dynamics of water in the mode-coupling theory.

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Despite the obvious relevance of liquid water in nature, many physical properties of this liquid are far from being fully understood. Of interest here are the numerous experimental, numerical, and theoretical efforts [1,2] that have been devoted to understanding the thermodynamic and dynamic anomalies of liquid water, as, for example, the apparent divergence of the transport properties in the supercooled liquid region. Different models have been proposed to explain these anomalies, and among them it is worth recalling (i) the existence of two distinct liquid phases and, therefore, of a liquid-liquid transition line between these two liquids [3,4], (ii) a singularity-free scenario in which the thermodynamic anomalies are related to the presence of structural "heterogeneities" [5], and (iii) the mode-coupling theory (MCT) [6] based scenario, where the anomalies are the results of a dynamical slowing down, similar to that observed in glass forming systems. On the numerical side, the MCT has been applied to water dynamics [7], suggesting that the critical slowing down can be described as a purely dynamical process; i.e., the interpretation of the observed anomalies in the transport properties does not require an underlying thermodynamic singularity. However, to settle the matter and, in particular, to discriminate among the previous models, further experimental efforts are needed. In this respect, a recent optical Kerr effect (OKE) experiment [8] seems to point toward a MCT-based interpretation of the dynamics in liquid water. This experiment indicates the existence of a well defined stretching ($\beta < 1$) of the measured correlation functions. The OKE technique, however, does not probe directly the density-density correlation function $F(Q, t)$ (the central quantity of the MCT) and—as recently demonstrated [9]—care must be taken in making a quantitative comparison between OKE data and MCT predictions. In this respect, a direct determination of $F(Q, t)$—or of its Fourier transform $S(Q, \omega)$, the dynamic structure factor—is highly desirable.

The present challenge, which MCT predictions pose to experimentalists, is thus the determination of the density autocorrelation function $F(Q, t)$ and its temperature dependence. For this function, the MCT foresees a stretched exponential behavior in the long time limit:

$$F(Q, t) \propto \exp-[t/\tau(Q, T)]^{\beta} \qquad (1)$$

where $\tau(Q, T)$ is the characteristic time of a structural (α) relaxation process and β is its stretching parameter, predicted to be less than unity. Moreover, according to MCT, $\tau(Q, T)$ follows a power law divergence as a function of temperature [6]:

$$\tau(Q, T) \propto (T - T_{\mathrm{MCT}})^{-\gamma}. \qquad (2)$$

Molecular dynamics simulations [7] have shown that the divergence temperature T_{MCT} of water has been estimated to be in the 220–230 K interval.

Although the density-density correlation function of water has been investigated by different spectroscopic techniques such as Brillouin light scattering (BLS) [10–12] and x-ray scattering (IXS) [13], Eqs. (1) and (2) have never been experimentally tested. This is basically due to the impossibility so far to match sound waves with inverse frequency comparable to the relaxation time of the liquid in the supercooled temperature region. In fact, one desires a large water sample at a temperature low enough to meet the condition of best visibility for the relaxation process [$\omega_p(Q)\tau(Q, T) = 1$, $\omega_p(Q)$ being the frequency of the sound waves probed in the experiment]. In typical visible light scattering experiments the probed sound waves lie in the ≈ 7 GHz region that—in order to satisfy the $\omega_p(Q)\tau(Q, T) = 1$ relation—corresponds to temperatures well below the supercooling limit. In the accessible T region, the BLS measurements probe sound waves with $\omega_p(Q) \ll 1/\tau(Q, T)$; therefore, a reliable value of τ cannot be extracted. On the contrary, the IXS experiments probe Q values so high that the best sensitivity condition is reached at high temperatures (where τ

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is in the picosecond range), too far from the interesting T region where the anomalies of water start to develop. Indeed, in the high T region accessible to IXS, the measured values of τ are described with an Arrhenius law and do not show tendency to diverge at finite T. Moreover, at high temperatures, MCT predictions do not apply. The stretching of relaxation should show its effect at lower temperatures which are, though, outside the best sensitivity of the IXS technique to water time scale.

In this Letter, we report new determination of the dynamic structure factor of liquid water performed by using a novel inelastic ultraviolet scattering (IUVS) technique. The use of a probe with an energy higher (3 times in the present experiment) than that usually employed in normal Brillouin light scattering allows one to exchange a larger Q, thus to probe higher frequency sound waves and—in the case of water—to reach the condition $\omega_p(Q)\tau(Q,T) = 1$ in the accessible supercooling temperature range (about 255 K in the present case). Close to this temperature, we find the unambiguous signatures of the structural relaxation process (Mountain peak, broadening of the Brillouin lines, etc.) and we reliably derive the relaxation time $\tau(Q,T)$. The temperature dependence of $\tau(Q,T)$ and the value of the stretching parameter β of the density-density correlation function—determined from the experimental data—show the features foreseen by the MCT, thus providing experimental evidence for the applicability of such a theory to a liquid such as water.

The experiment was performed at the new IUVS beam line at the Elettra Synchrotron light laboratory in Trieste. Given the uniqueness of the setup, the experimental aspects will be discussed in some detail. The source, a figure-eight undulator with a period of 140 mm [14,15], was used in first harmonic where it produces ultraviolet radiation in the 5–11 eV range with a flux of $\approx 10^{15}$ photons/s/0.1% BW. The beam coming from the source is "cleaned" from short wavelength radiation and focused down to 50 μm to the entrance slit of the monochromator by three successive reflections [16]. The Czerny-Turner [17] normal incidence mirror optical design has been chosen for the monochromator. In this design, light from the entrance slit is rendered parallel by a spherical concave mirror and reflected onto an *echelle* plane grating. The diffracted beams are then refocused by a second spherical mirror onto the exit slit. This design has the most desirable features when working below 11 eV, namely, resolution, high light-gathering power, scanning mechanism, and the advantages of fixed exit and entrance slits with no deviation in the direction of the exit beam. The relative energy resolution, assuming negligible the intrinsic contribution coming from the grating, is given by $\delta\cot(\phi)/2F$, where δ is the slit opening, F is the focal length of the spherical mirrors, and ϕ is the grating blaze angle. We built an 8 m focal length monochromator with a 70° grating blaze angle to match the best compromise between needed resolving power (10^6 or better) and mechanical feasibility [16]. Once monochromatized, the beam is focused onto the sample with a spot size of about $100 \times 100\ \mu\text{m}^2$. A spherical mirror is used to collect the radiation scattered from the sample over a solid angle of $40 \times 40\ \text{mrad}^2$ and send it to the entrance slit of a second 8 m Czerny-Turner spectrograph that, in this case, is used to analyze the scattered intensity. The photons are detected by a 13.5 μm pixel CCD detector, which allows collection of the inelastic spectrum in one single shot, thus avoiding long-lasting monochromator scans of the diffraction angle.

The momentum transfer can be varied by changing the scattering angle θ and depends on the refraction index of the sample n via the relation: $Q = 4\pi n/\lambda \sin(\theta/2)$, λ being the incident photon wavelength. In our measurements θ was set to 176°. The overall relative energy resolution, measured using a copper surface as an isotropic scatterer, is 2×10^{-6}, a value very close to the theoretical limit (1.7×10^{-6}).

The water sample was high purity H_2O kept in a 10 mm long Suprasil cell sealed in an argon atmosphere. The sample temperature was changed in the range from 343 down to 260 K. The absence of impurities was checked by looking at the intensity transmitted by the sample up to 7.5 eV where the absorption of water becomes dominant [18]. The incident photon energy was fixed to 6.75 eV (at this energy the absorption length for water is several centimeters) and the spectra were taken in the range $\pm 500\ \mu$eV with a CCD detector. The CCD noise was reduced to 1 electron/pixel/hour by cooling the chip to 190 K; the spectrum was obtained by integrating over a strip 0.13 mm long orthogonal to the grating dispersion direction. The total integration time for each spectrum was 120 s, giving rise to a total intensity of $\approx$ 50 photons/channel.

In Fig. 1 we show a set of representative IUVS spectra of liquid water that indicates the quality of the spectra and the feasibility of inelastic ultraviolet scattering experiments. The spectra show a clear broadening of both the Brillouin peaks and the central line, which is not resolution limited as emphasized by superimposing the resolution function on the spectrum at 302.5 K. The spectra also show the presence of a contribution (narrow and centered close to zero energy) coming from the sample cell surface reflection. In order to extract quantitative information from the IUVS spectra such as those shown in Fig. 1, we model the shape of the dynamic structure factor according to the memory function formalism [19]. Within this framework, the dynamic structure factor can be written as

$$S(Q,\omega) = \frac{2c_o^2 Q^2}{\omega} \mathrm{Im} \frac{1}{\omega^2 - \omega_o^2 - i\omega\tilde{M}(Q,\omega)}. \qquad (3)$$

Here c_o is the adiabatic sound speed and $\tilde{M}(Q,\omega)$ is the Fourier transform of the density-density second memory

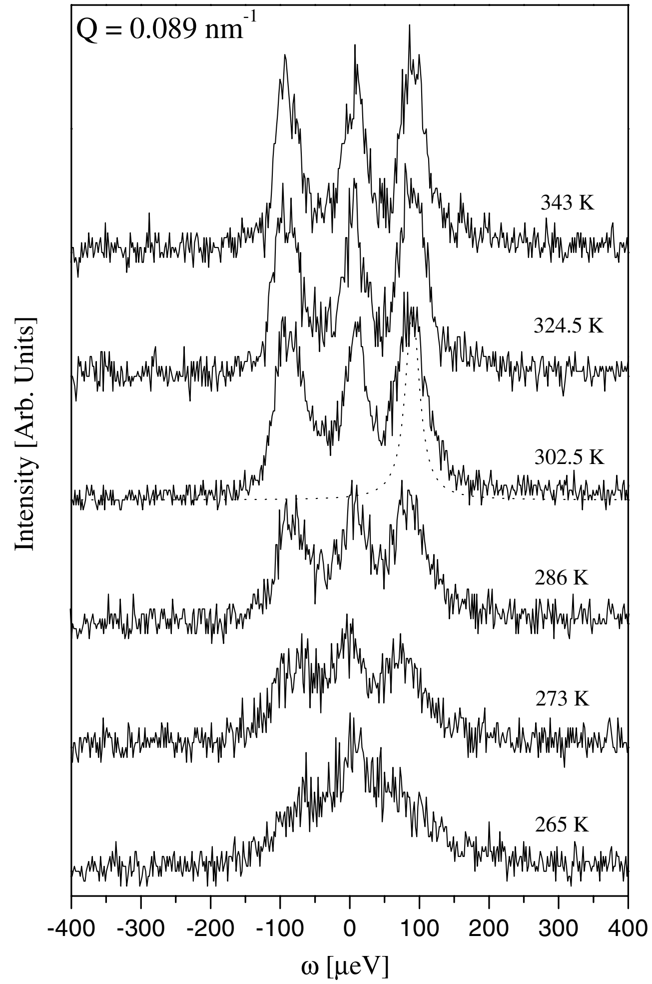

FIG. 1. Examples of inelastic UV scattering spectra of liquid and supercooled water, taken with 6.75 eV incident photon energy and 0.089 nm^{-1} momentum transfer, at the indicated temperatures. For comparison, the overall instrumental resolution function is superimposed on the spectrum at 302.5 K, shifted and aligned with the Stokes Brillouin line.

function. To model this memory function, we choose—beside the thermal contribution—a stretched exponential function to describe the relaxational part of the memory function and a Markovian term to represent the microscopic decay [13].

$$M(Q, t) = \omega_o^2(\gamma_c - 1)e^{-D_T Q^2 t} + 2\gamma_o \delta(t) + \Delta^2 e^{-(t/\tau)^\beta}, \tag{4}$$

where γ_c is the specific heat ratio C_P/C_V, D_T is the thermal diffusivity coefficient, γ_o accounts for the "microscopic contribution," and $\Delta^2 = Q^2(c_\infty^2 - c_o^2)$ is the structural relaxation strength. Moreover, c_∞ is the infinite frequency speed of sound and β is the stretching parameter. In the framework of the idealized MCT [6] β is temperature independent and ≤ 1. The function used to fit the data is given by the convolution

$$I(Q, \omega) = R(\omega) \otimes [C(\omega) + S(Q, \omega)], \tag{5}$$

where $R(\omega)$ is the experimentally determined resolution function and $C(\omega)$ represents the empty cell contribution to the spectra (basically an off-center δ function).

We have fitted the experimental data to Eqs. (3)–(5), after the subtraction of the detector dark current. The fit procedure has been performed by standard χ^2 minimization, and the χ^2 values obtained were always within 1 standard deviation from the expected value. The values of D_T, γ, and c_o have been fixed to those reported in [13] and references therein. As an example, in Fig. 2 we show the result of the fitting procedure for the spectra at 343 and 269 K.

The values obtained for the relaxation time are displayed in Fig. 3. The comparison with IXS [13] shows that the relaxation time for temperatures above room temperature is in good agreement with IXS studies, while there is a clear non-Arrhenius behavior as soon as the temperature is lowered below 280 K, i.e., when the IXS values are less reliable. In the inset in Fig. 3 we show the temperature dependence of the stretching parameter. We observe that, within the error bar, β does not show a significant temperature dependence, in agreement with the MCT predictions. As anticipated before, according to the MCT, the characteristic relaxation time of a supercooled liquid approaching the glass transition is proportional to $(T - T_{\mathrm{MCT}})^{-\gamma}$, where T_{MCT} is the critical temperature marking the ergodic to nonergodic transition behavior

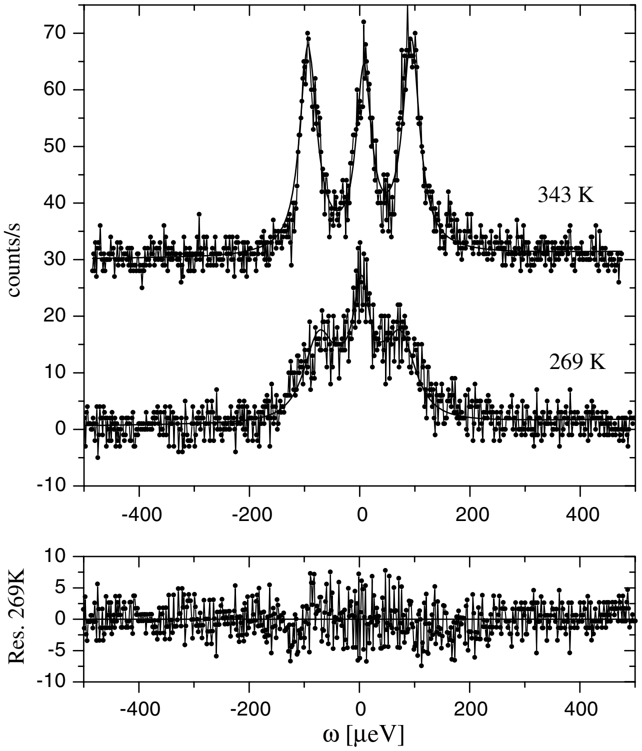

FIG. 2. Examples of fits (solid lines) of the spectra at $T = 343$ K and $T = 269$ K. The experimental data are superimposed on the fit (solid line). Residuals at 269 K are also shown in the lower panel.

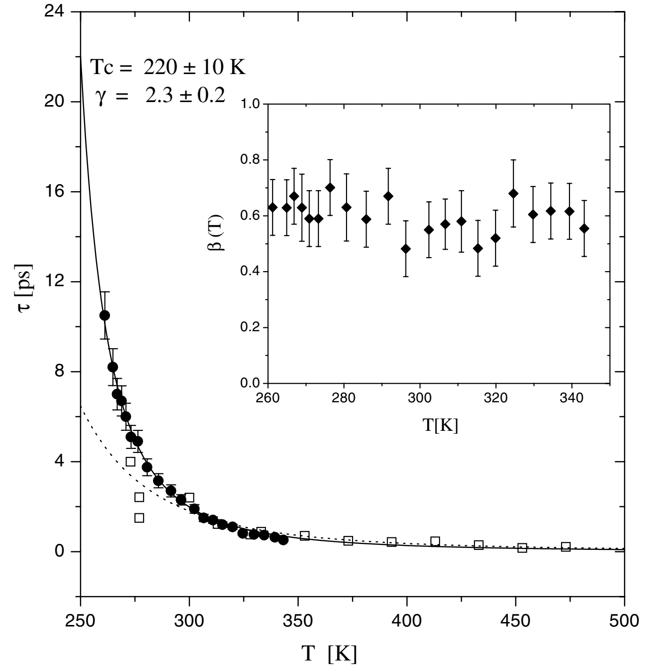

FIG. 3. Temperature dependence of the structural relaxation time τ as obtained by fitting the experimental data to Eqs. (3)–(5) (solid circles). For the sake of comparison, IXS [13] data are also shown (open squares). The solid line represents the MCT theory prediction [6] fitted over the displayed experimental points. We have obtained $T_{\mathrm{MCT}} = 220 \pm 10$ K and $\gamma = 2.3 \pm 0.2$. The dotted line represents the Arrhenius behavior inferred in [13]. In the inset we report the T dependence of the structural stretching parameter β (solid diamonds).

of density fluctuations and γ is the critical exponent. Aiming to extract reliable values for γ and T_{MCT}, we fitted together the τ data from both the present IUVS and previous IXS experiments [13]. We get $T_{\mathrm{MCT}} = 220 \pm 10$ K and $\gamma = 2.3 \pm 0.2$, values in very good agreement with MCT theory and simulations [7]. Therefore, the temperature independence of β and the values obtained for T_{MCT} and γ strongly support the MCT idea that describes the slowing down of the dynamic properties of water relaxing the need of a thermodynamic critical behavior.

In conclusion, we have reported an inelastic ultraviolet scattering measurement of the dynamic structure factor of water in the temperature range where the divergence of the transport quantities starts to be relevant. In the supercooled temperature region, IUVS provides an accurate determination of the relaxation parameters showing a non-Arrhenius behavior of the structural relaxation time. Good agreement with the idealized MCT is obtained, showing that the origin of the divergence at $T_{\mathrm{MCT}} \approx 220$ K can be related to dynamical properties of the system. This strongly supports the idea that at ambient pressure the divergence of the relaxation time τ can be explained without resorting to an underlying thermodynamic singularity. Finally, these results show the ability of inelastic UV scattering to study the collective dynamics of liquids and, more specifically, the structural relaxation in hydrogen-bonded systems where the "best sensitivity" condition is matched.

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