Is There Any Fast Sound in Water?

S. C. Santucci,[1,2,3] D. Fioretto,[2,3] L. Comez,[2,3] A. Gessini,[1] and C. Masciovecchio[1]
[1]*Sincrotrone Trieste, s.s. 14, km 163.5, 34012 Basovizza, Trieste, Italy*
[2]*Dipartimento di Fisica, Università di Perugia, Via Pascoli, 06100 Perugia, Italy*
[3]*CRS SOFT-INFM-CNR, c/o Università di Roma La Sapienza, 00185 Roma, Italy*
(Received 3 October 2006; published 27 November 2006)

We measured the dynamic structure factor $S(Q, \omega)$ of liquid and undercooled water down to 253 K in the $Q \approx 0.02$–$0.1\ \mathrm{nm}^{-1}$ momentum transfer region. We observe the neat departure of the apparent speed of sound from the adiabatic regime as a function of decreasing temperature. Our evaluation of the infinite-frequency limit of sound velocity, c_∞, matches with the results obtained in the high momentum transfer limit by inelastic neutron and x-ray scattering. These results strongly support the viscoelastic interpretation of the dynamics of water. Hence, we propose to call c_∞ the high-frequency speed of sound and to abandon the term fast sound, which recalls a propagation mechanism through lighter atoms, like in gas mixtures.

DOI: 10.1103/PhysRevLett.97.225701 PACS numbers: 64.70.Pf, 61.20.Qg, 62.60.+v, 78.40.Dw

Intriguing properties of water, such as a negative melting volume, density maximum in the normal liquid range, and divergence of transport properties in the undercooled phase, have been stimulating a massive production of theoretical interpretations and experimental studies for decades [1–3]. Among the debated issues, a fascinating question is about the nature of the acousticlike mode existing at wave vectors higher than 1 nm^{-1} and propagating at about 3200 m/s, a value close to the speed of sound in ice and roughly twice than that of ordinary sound in the liquid [4].

The first indication of the presence of such a high-frequency sound mode was given in 1974 by molecular dynamics (MD) simulations [5]. A decade later, inelastic neutron scattering (INS) experiments on D_2O provided the first experimental evidence for a collective mode having a speed of ≈ 3300 m/s in the $Q = 3.5$–$6\ \mathrm{nm}^{-1}$ region [6]. In the same years, the term fast sound was introduced to indicate a high-frequency ($\omega/2\pi \approx 10^{13}$ Hz) and high Q's (≈ 1–$6\ \mathrm{nm}^{-1}$) density wave that was calculated by MD [7] and detected by INS [8] in binary mixtures with large mass difference, like metallic alloys and rare-gas mixtures. This fast mode was inferred to be propagated by the lighter component of the mixture alone [9]. Moreover, MD simulations suggested a bifurcation from normal to fast-sound regime at wave vectors approaching some nm^{-1} [10]. The denotation fast sound was progressively extended to the high-frequency sound found in water [11] when MD studies attributed its propagation to the librational motion of hydrogen atoms [12].

Nevertheless, to date, the physical origin of fast sound in water is still a matter of debate. Two phenomenological models are currently in use to describe the whole amount of INS and inelastic x-rays scattering (IXS) spectra of water, collected during last years: (i) the viscoelastic model [13–15] which attributes the dispersion of apparent speed of sound, between the low frequency limit of ≈ 1500 m/s and the high-frequency limit of ≈ 3200 m/s, to the occurrence of the structural relaxation in the picoseconds time scale; and (ii) the interaction model [16], conceived in conceptual agreement with the hydrodynamics of disparate-mass fluid mixtures [9], which hypothesizes the existence of an acoustic and of an opticlike mode, having the same symmetry and repelling each other at $Q \approx 4\ \mathrm{nm}^{-1}$. In this picture, the fast sound is associated to the steeper slope of acoustic branch after the interaction.

A resource for the settlement of an unambiguous interpretation is the measurement of density fluctuations in the low momentum transfer region, namely, below 1 nm^{-1}, in the hydrodynamic limit. At low Q's, in fact, the symmetry rules decouple longitudinal from transverse variables in the generalized Langevin equations [17]: i.e., pure longitudinal and transverse modes should be detected separately. Brillouin light scattering (BLS) technique, operating at Q's $\approx 0.03\ \mathrm{nm}^{-1}$, was employed in the past to study the viscoelastic behavior of water [18] but it had to face the problem of sample crystallization before reaching the temperature where a significative departure from normal sound should be observed.

The novel inelastic ultraviolet scattering (IUVS) technique [19] extends the explorable Q region from 0.03 up to $\approx 0.1\ \mathrm{nm}^{-1}$, providing new crucial information about water dynamics.

In this Letter we present low momentum transfer measurements of the dynamic structure factor $S(Q, \omega)$ of liquid and undercooled water, carried out by BLS down to 251 K and by IUVS down to 253 K. Combined analysis of same-temperature spectra taken at different Q's gives decisive evidences in favor of viscoelastic interpretation of the nature of high-frequency sound velocity in water.

We used samples of class-A ultrapure water. IUVS experiments were performed at the Beamline 10.2 of the Elettra Synchrotron Light Laboratory [19]. Spectra were acquired for incident energies of 6.72, 6.2, and 5.1 eV, corresponding, respectively, to $Q = 0.0994$, $Q = 0.0896$, and 0.0712 nm^{-1}, and at temperatures ranging from 343 down to 253 K, where crystallization occurred. The overall experimental resolution was ~5.6 GHz. BLS experiments were done in both 90° ($Q = 0.0229\ \mathrm{nm}^{-1}$) and backscattering ($Q = 0.0326\ \mathrm{nm}^{-1}$) geometries, using a 514.5 nm Ar^+ laser source and a Sandercock setup [20]. Density fluctuation spectra were obtained from polarized and depolarized spectra, following the procedure described in [21]. The experimental resolution was 150 MHz [20], better than previous BLS experiments in water [18], due the use of a triple-pass tandem setup that eliminates the superposition of higher orders and considerably increases the contrast [20].

In Fig. 1 we show a selection of spectra, which summarizes the whole experiment. The evident broadening of inelastic peaks as a function of decreasing temperature is interpreted, in the viscoelastic model, as the typical feature of a relaxation process, evolving on a time scale that matches the reciprocal frequency of the longitudinal modes. In this framework, as a function of decreasing temperature or increasing Q, the structural relaxation drives the transition of the apparent sound velocity $C(T, Q)$ of the longitudinal mode between the adiabatic limit, c_0, and high-frequency limit c_∞ [1]. We evaluated $C(T, Q) = \Omega(T, Q)/Q$, where Ω corresponds to the maximum of the current $I = \omega^2 S(Q, \omega)$. In the lower panel of Fig. 2 we report $C(T, Q)$ as a function of temperature for each investigated Q. At high temperatures $C(T) \approx c_0$, that is, water dynamics is in its adiabatic limit ($\omega\tau \ll 1$). Neat incipit of the expected transition is evident, in each Q series, as a function of decreasing temperature, as well as lower departure temperature for lower Q's.

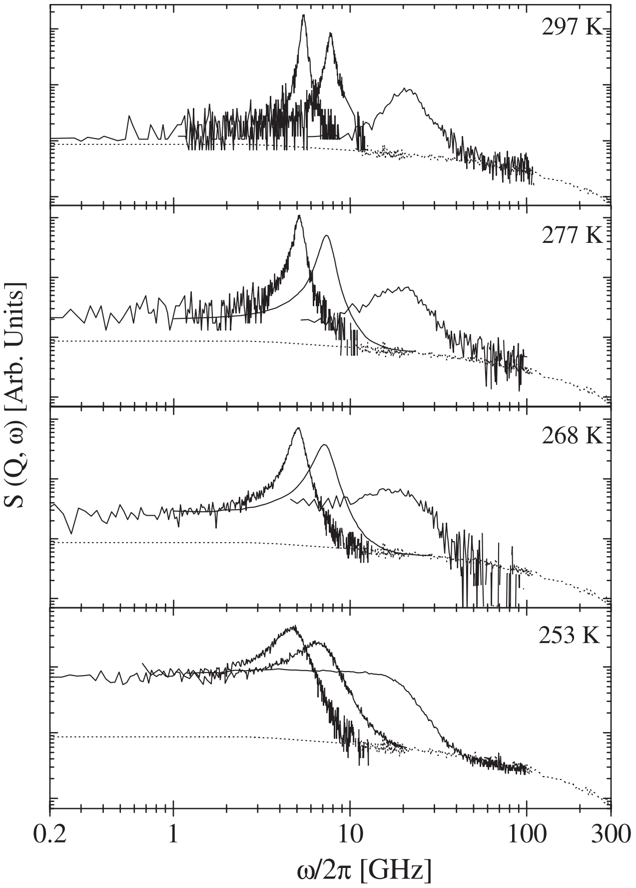

FIG. 1. Stokes side of Brillouin spectra at 297, 277, 268, and 253 K and $Q = 0.0229$, 0.0326, 0.0896 nm^{-1} (except for $T = 253$ K, where the $Q = 0.0712\ \mathrm{nm}^{-1}$ spectrum is shown), in both the VV (vertical polarization selected for both incoming and outgoing radiation) (solid lines) and VH (vertically polarized incoming radiation and horizontal outgoing) (dotted lines) configurations.

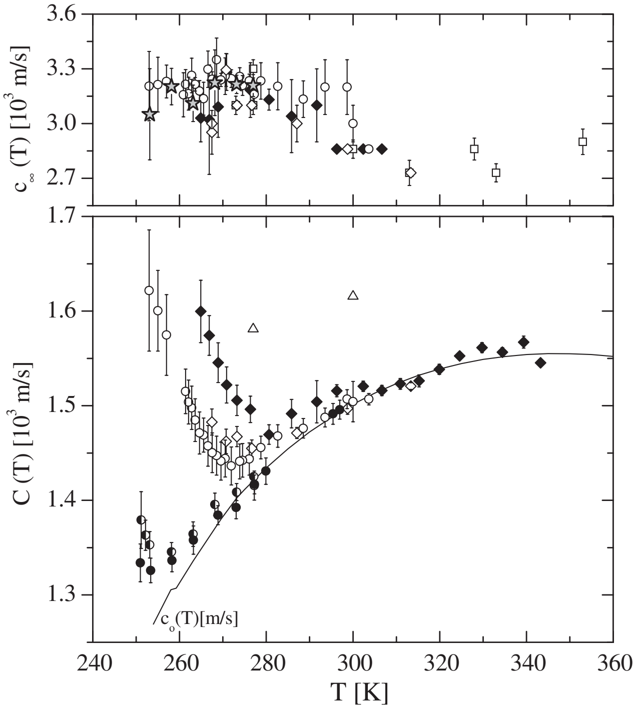

FIG. 2. Upper panel: high-frequency limit of sound velocity, $c_\infty(T)$, obtained by viscoelastic analysis of BLS and IUVS spectra with Eq. (1). Open star result from joint-fitting procedure, full diamonds from $Q = 0.0994\ \mathrm{nm}^{-1}$ spectra; open diamonds from $Q = 0.0896\ \mathrm{nm}^{-1}$ and open circles, from $Q = 0.0712\ \mathrm{nm}^{-1}$ spectra. Open squares are IXS data [14]. Lower panel: full line represents the low frequency limit of sound velocity as a function of temperature, $c_0(T)$, from ultrasonic measurements [24]. Dots represent the apparent sound velocity, $C(Q, T)$, evaluated from the maximum density of current of spectra taken at different Q's in this work. The departure from ultrasonic behavior can be observed at ≈300 K for $Q = 0.0994\ \mathrm{nm}^{-1}$ (IUVS, full diamonds), at ≈284 K for $Q = 0.0896\ \mathrm{nm}^{-1}$ (IUVS, open diamonds), at ≈280 K for $Q = 0.0712\ \mathrm{nm}^{-1}$ (IUVS, open circles), at ≈265 K for $Q = 0.0326\ \mathrm{nm}^{-1}$ (BLS, half full circles), and at ≈269 K for $Q = 0.0229\ \mathrm{nm}^{-1}$ (BLS, full circles). Open triangles represent the prediction of the interaction model at $Q = 0.0994\ \mathrm{nm}^{-1}$.

We stress that this is the first report about the detachment of $C(T)$ from c_0 in undercooled water, at the Q's ≈ 0.1 nm^{-1} probed by IUVS technique. Indeed, below ≈ 300 K, this novel technique satisfies the condition for best visibility of the structural relaxation of water, $\omega_P \tau \approx 1$, where ω_P is the probed mode and τ the relaxation time.

The apparent sound velocity can be directly compared to the prediction of the interaction model. We compared $C(T, Q)$ measured at $Q = 0.0994$ nm^{-1}, $T = 300$ and $T = 277$ K, to the corresponding values calculated according to Ref. [16]. Results are shown in the lower panel of Fig. 2 as open triangles. At $T = 300$ K, the interaction model gives $C = 1615$ m/s, which overestimates the measured value, 1518 m/s, of 7%; while at $T = 277$ K, it provides $C = 1581$ m/s, which overestimates the measured value, 1486 m/s, of 6%. Even if authors themselves advise that their phenomenological model should not be extended over its range of validity, the discrepancies we found at $Q \approx 0.1$ nm^{-1} seem to suggest that a too strong coupling might have been supposed in [16] between acoustic and optic modes, at low Q's.

The high-frequency limit values of sound velocity, $c_\infty(T)$, are reported in upper panel of Fig. 2. They have been evaluated by a full-spectrum viscoelastic analysis, with the following line shape for $S(Q, \omega)$ [17]:

$$S(Q, \omega) = \frac{2c_0^2 Q^2}{\omega} \operatorname{Im}\left\{\frac{1}{\omega^2 - \omega_0^2 - i\omega\tilde{M}(\omega)}\right\}. \quad (1)$$

Here, c_0 is the adiabatic sound velocity, $\omega_0 = c_0\, Q$, and $\tilde{M}(\omega)$ is the memory function in the frequency domain. $\tilde{M}(\omega)$ is the sum of three terms: the instantaneous response, the thermal relaxation, and the stretched structural relaxation, related to the viscosity.

Thermal and instantaneous contribution in $\tilde{M}(Q, \omega)$, the last being smaller than the experimental resolution in any case, were fixed to the values given in [14] and references therein.

Water has stretched relaxation [22] shaped, at given T and Q, by a Cole-Davidson function [23] $m^*(\omega) = -(iQ^2/\omega)\Delta^2[1 - 1/[1 + i\omega\tau]^\beta]$, where $\Delta^2 = c_\infty^2 - c_0^2$ is the relaxation strength, c_∞ is the infinite-frequency limit of sound velocity, and τ and β are the relaxation time and the stretching parameter. Since we are in the hydrodynamic limit, the Q dependence of these parameters can be neglected [14]. Hence, contemporary fitting of Eq. (1) convoluted with the experimental resolution has been performed on couples or triplets of spectra taken at the same temperature and different Q's.

We used a Levemberg-Marquardt routine which minimizes the sum of χ^2's relative to spectra involved, and keeps c_0, c_∞, τ, and β as common parameters, holding c_0 fixed to the adiabatic sound values measured by ultrasonic techniques [24]. In Fig. 3 we show spectra measured at 273 K with fitting lines of joint analysis superimposed.

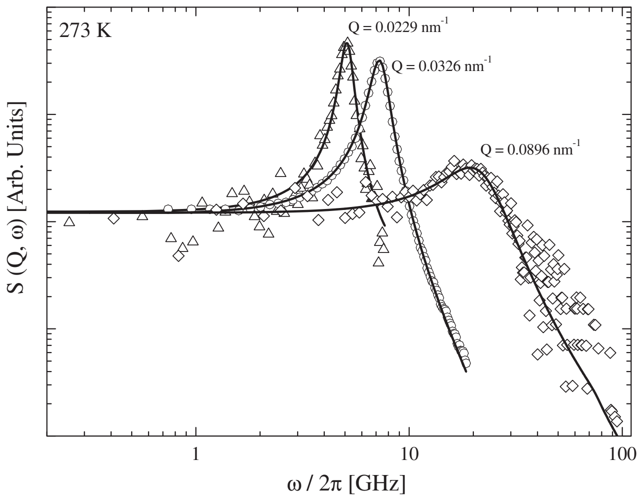

FIG. 3. Stokes peaks of spectra taken at 273 K and $Q = 0.0229$, 0.0326, 0.0896 nm^{-1}, with the respective fitting lines of joint analysis with viscoelastic line, Eq. (1), superimposed.

The joint-fitting procedure is the qualifying point of this analysis, because it gives us access to a two decades wide frequency window, large enough to map the memory function of undercooled water. In a preliminary work, carried out by IUVS technique alone [25], we gave decisive evidences in favor of the mode-coupling theory predictions about the dependence of τ on temperature, in agreement with results obtained by optical Kerr effect [22] and neutron spin echo [26] measurements. In the present work important improvements were done, respect to the previous one, in order to determine the temperature behavior of c_∞. In particular, besides the exploration in a twice wide frequency window, we were also able to cool the sample below the previous limit. Moreover, we got noticeable improvement of the statistics and twice better resolution.

Values of $\tau(T)$ and $\beta(T)$ confirm the previous work. The most striking result is the determination of c_∞ in the dynamic window where the relaxation of water occurs. $c_\infty(T)$ from joint analysis is reported as stars in Fig. 2. Spectra having no same-temperature partner have been fitted constraining β in the range obtained by joint analysis (dots, in Fig. 2). We got $c_\infty = 3200 \pm 100$ m/s, almost constant in the whole range of temperature. Our values are consistent with the IXS results taken in the 1–8 nm^{-1} regime [14]. This agreement testifies that the speed of sound measured at high frequency corresponds to the relaxation-free limit of sound modes, as universally observed in glass-forming materials.

In conclusion, we have investigated the dynamics of liquid and undercooled water from 343 down to 253 K, in the 0.02–0.1 nm^{-1} momentum transfer region, where acoustic and opticlike modes are well separated. In this work we have provided two main evidences: (i) the neat departure of the apparent speed of sound $C(Q, T)$ from the ultrasonic limit c_0 towards c_∞ as a function of decreasing temperature; (ii) the agreement between the infinite-frequency sound velocity, c_∞, evaluated at $Q \approx 0.1\ \mathrm{nm}^{-1}$, and the values found by IXS in the 1–7 nm^{-1} region [14]. These features are universally observed in glass-forming systems when the transition from the viscous to the elastic regime takes place, driven by the occurrence of the structural relaxation process. For these reasons we suggest to abandon the use of the term fast sound, which recalls a propagation mechanism through lighter atoms of gas mixtures, and to retrieve the original high-frequency sound denotation of c_∞, appropriate to unambiguously identify the relaxational origin of free density fluctuations in water.

We also wish that the progressive understanding of water dynamics will favor the clarification of similar phenomena occurring in a variety of systems, like protein hydration water [27] and expanded fluid Hg at the metal-nonmetal transition [28].

We are grateful to B. Sartori for her technical support.

[1] P. G. Debenedetti, *Metastable Liquids* (Princeton University, Princeton, NJ, 1997).
[2] C. A. Angell, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1981), Vol. 7.
[3] O. Mishima and H. E. Stanley, Nature (London) **396**, 329 (1998).
[4] G. Ruocco and F. Sette, J. Phys. Condens. Matter **11**, R259 (1999).
[5] A. Rahman and F. H. Stillinger, Phys. Rev. A **10**, 368 (1974).
[6] J. Teixeira, M. C. Bellissent-Funel, S. H. Chen, and B. Dorner, Phys. Rev. Lett. **54**, 2681 (1985).
[7] G. Jacucci, M. Ronchetti, and W. Schirmacher, J. Phys. (Paris), Colloq. **8**, 385 (1984); J. Bosse, G. Jacucci, M. Ronchetti, and W. Schirmacher, Phys. Rev. Lett. **57**, 3277 (1986).
[8] W. Montfrooij, P. Westerhuijs, V. O. de Haan, and I. M. de Schepper, Phys. Rev. Lett. **63**, 544 (1989); M. Alvarez, F. J. Bermejo, P. Verkerk, and B. Roessli, Phys. Rev. Lett. **80**, 2141 (1998).
[9] E. Enciso, N. G. Almarza, M. A. Gonzalez, F. J. Bermejo, R. Fernandez-Perea, and F. Bresme, Phys. Rev. Lett. **81**, 4432 (1998).
[10] M. Sampoli, U. Bafile, E. Guarini, and F. Barocchi, Phys. Rev. Lett. **88**, 085502 (2002).
[11] F. Sette, G. Ruocco, M. Krish, U. Bergmann, C. Masciovecchio, V. Mazzacurati, G. Signorelli, and R. Verbeni, Phys. Rev. Lett. **75**, 850 (1995).
[12] M. A. Ricci, D. Rocca, G. Ruocco, and R. Vallauri, Phys. Rev. Lett. **61**, 1958 (1988).
[13] F. Sciortino and S. Sastry, J. Chem. Phys. **100**, 3881 (1994).
[14] G. Monaco, A. Cunsolo, G. Ruocco, and F. Sette, Phys. Rev. E **60**, 5505 (1999).
[15] E. Pontecorvo, M. Krish, A. Cunsolo, G. Monaco, A. Mermet, R. Verbeni, F. Sette, and G. Ruocco, Phys. Rev. E **71**, 011501 (2005).
[16] C. Petrillo, F. Sacchetti, B. Dorner, and J.-B. Suck, Phys. Rev. E **62**, 3611 (2000); F. Sacchetti, J.-B. Suck, C. Petrillo, and B. Dorner, Phys. Rev. E **69**, 061203 (2004).
[17] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (Dover, New York, 1991).
[18] A. Cunsolo and M. Nardone, J. Chem. Phys. **105**, 3911 (1996).
[19] C. Masciovecchio, D. Cocco, and A. Gessini, *Proceedings of the Eighth International Conference of Synchrotron Radiation, S.R.I., 1993* (AIP, Warwick, 2004), p. 1190.
[20] F. Nizzoli and J. R. Sandercock, in *Dynamical Properties of Solids*, edited by G. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1990).
[21] D. Fioretto, L. Comez, G. Socino, L. Verdini, S. Corezzi, and P. A. Rolla, Phys. Rev. E **59**, 1899 (1999).
[22] R. Torre, P. Bartolini, and R. Righini, Nature (London) **428**, 296 (2004), and references therein.
[23] C. P. Lindsey and G. D. Patterson, J. Chem. Phys. **73**, 3348 (1980).
[24] J. C. Bacri and R. Rajaonaris, J. Phys. Lett. (Les Ulis) **40**, 2404 (1979); V. A. Del Grosso and C. W. Mader, J. Acoust. Soc. Am. **52**, 1442 (1972); W. Wagner and A. Pruß, J. Phys. Chem. Ref. Data **31**, 387 (2002).
[25] C. Masciovecchio, S. C. Santucci, A. Gessini, S. Di Fonzo, G. Ruocco, and F. Sette, Phys. Rev. Lett. **92**, 255507 (2004).
[26] M. C. Bellissent-Funel, S. Longeville, J. M. Zanotti, and S. H. Chen, Phys. Rev. Lett. **85**, 3644 (2000).
[27] M. Tarek and D. J. Tobias, Phys. Rev. Lett. **89**, 275501 (2002).
[28] D. Ishikawa, M. Inui, K. Matsuda, K. Tamura, S. Tsutsui, and A. Q. R. Baron, Phys. Rev. Lett. **93**, 097801 (2004).