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hypersurface to the product side. This is an example of one possible aspect of transition-state behavior that is not analogous to the aspects of reactant and product structure considered in the above analysis of contributions to our observed DIE on an NEIE. A second special aspect of transition-state behavior could, in principle, also contribute to an IE on a KIE; variational transition-state theory suggests that isotopomeric transition states could occur at significantly different points along the reaction path.³⁷

Calculations by Huskey and Schowen³⁸ have shown that observed^{39,40} DIEs on DKIEs for hydride transfers can be explained by tunneling, and their explanation has been invoked for two later observations^{41,42} of related DIEs on DKIEs. Similar calculations by Saunders⁴³ have shown that DIEs on DKIEs and TKIEs observed⁴⁴ for elimination reactions imply tunneling. For use of observed IEs on KIEs as evidence for tunneling or for any other behavior that is peculiar to transition states, it is necessary to show

that the observation could not arise from an origin analogous to that presented here to account for the DIE on the NEIE for eq 1 (participation of both isotopic atoms in a high-frequency vibrational mode of the reactant, $C_5H_5NL^+$). The above cited calculations have done that, and Huskey and Schowen, in particular, emphasized that for the hydride-transfer activation process they modeled, such coupled motion of the two isotopic L's is present both in the reactant and in the transition state, and contributions from those two structures to a DIE on the DKIE largely cancel. Such cancellation cannot occur in the DIE on the NEIE for eq 1, because the two isotopic atoms are in separate molecules in the products ($L_3O^+ + C_5H_5N$). Similarly, significant DIEs on DEIEs are observed for equilibria such as eq 8 because the two isotopic L's are in separate molecules in the reactants and in the same molecule in the products.

In summary, DIEs either on DKIEs or on heavy-atom KIEs are likely to be observed even in the absence of tunneling if two conditions are satisfied: (1) if the two isotopic atoms in the transition state were initially in separate reactant molecules, and (2) if motion of both isotopic atoms contributes to at least one vibrational mode of the transition state for which $h\nu/k_bT$ has a value significantly greater than 2. Careful model calculations are required before an observed IE on a KIE can be attributed with confidence to any aspect of structure or behavior that is peculiar to transition states.

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Relaxation Process in Deeply Supercooled Water by Mandelstam-Brillouin Scattering†

S. Magazù, G. Maisano, D. Majolino, F. Mallamace, P. Migliardo,*

Dipartimento di Fisica dell'Universita' and CISM-GNSM del CNR, Universita' di Messina, Contrada Papardo, PO Box 55, 98010 S. Agata, Messina, Italy

F. Aliotta, and C. Vasi

Istituto di Tecniche Spettroscopiche del CNR, Contrada Papardo, PO Box 55, 98010 S. Agata, Messina, Italy
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Polarized Mandelstam-Brillouin scattering data in bulk supercooled water are presented. The hypersonic velocity and absorption are measured as a function of the scattering angle θ at temperatures ranging from +20 to -27.4 °C. The experimental results indicate the existence of a relaxation process in the gigahertz region. We discuss the observed dispersion in the frame of the relaxation theory for moderately supercooled liquids. The obtained relaxation times and relaxation strengths are interpreted in terms of many-body effects involved to explain the behavior of supercooled water.

General Considerations

The investigation of physical and chemical quantities in metastable supercooled water, where anomalous behaviors have been discovered,^{1,2} gives the opportunity of gaining more insight into the complex nature of this fundamental system. Very refined experiments concerning the structure and the dynamics^{3,7} of water as well as new theoretical models⁸⁻¹² and new molecular dynamics calculations¹³⁻¹⁶ furnished evidence that the aggregative phenomena occurring in the liquid near melting point are enhanced when subzero temperatures are reached. This gives rise to a hierarchy of structural environments (the so called *inherent structures* of Stillinger and Weber⁸) evolving within a very large time range extending from the subpicosecond to the nanosecond

scale.⁷ It is well-known⁶⁻¹⁷ that the making and the breaking process of the hydrogen bond is the fast elementary rate step. This

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primitive dynamical process, with the tendency of the H_2O molecules to aggregate (because the 1:1 ratio of its donor to acceptor groups¹⁸) in a near tetrahedral configuration allows the generation of extended fluctuating structures. When the temperature is lowered in the supercooled region, the system looks more and more like a *locally structured transient gel*. In this respect, liquid water behaves like an associated liquid exhibiting diffusional relaxation processes. Their characteristic times (residence time, jumping time, etc.) have recently been measured as a function of the temperature by quasi-elastic neutron-scattering experiments.⁵ As far as the specific description of the random network topology in supercooled water is concerned, MD calculations very recently furnished evidence of the possible existence of H-bonded rings,^{8,12,15} particularly pentagons and hexagons, whose concentration numbers increase when the temperature decreases. Furthermore, the organization of these rings in polyhedra gives rise to low-density icelike structures (for the hexagons), whereas the pentagons organize themselves into polyhedra that are mainly present in low-density amorphous ice. Since the structure created by the pentagons is topologically favorable and tends to be *autocatalytic*,⁸ the limit structure to which the supercooled water tends could be the amorphous form of ice,⁴ not the crystalline one. In addition, the *critical singularity*¹ at the supercooling limit, shown by many thermodynamical and transport quantities, can be due to a superarrangement of the tetrahedral units in H-bonded polyhedra with a longer than 10-Å extent. Besides these superarrangements, the presence of some antistructural units, mainly hydrophobic cavities (clathrate-like), has been observed in water. The diffusion of these defects in the water network can originate microscopic dynamical processes with subsequent relaxation phenomena.¹²

Brillouin scattering spectroscopy offers a powerful tool to investigate relaxation processes in liquids.¹⁹ Recently, the presence of a relaxation process in the gigahertz frequency region in supercooled water has been postulated to explain some results concerning the analysis of the hydrodynamic triplet.²⁰ In particular the hypersonic velocity v_s and absorption α/f^2 extracted by the dynamical structure factor $S(k, \omega)$ shows an anomalous behavior in the temperature range from -20 to -27 °C. The velocity shows a well-defined minimum at about -22 °C, whereas the absorption tends to flatten. This event, together with the indication that our measured absorption is well above the calculated $(\alpha/f^2)_{\text{classical}}$, ensures that we are in presence of a relaxational acoustic phenomenon. Nevertheless, by performing a comparison between our velocity data and the few existing experiments below -20 °C performed on *unusual* samples (small droplets²¹ at 54 kHz and thin films²² at 925 MHz), we had some difficulties in fully explaining the acoustic behavior. In effect, the velocity data at a lower frequency (ultrasonic) show a clear trend to flatten in the range from -25 to -33 °C rationalized by the authors as due to a heterophase fluctuation.²¹ On the other hand, the data at 925 MHz show a monotonic decrease down to -26 °C and seem to be inconsistent with the ultrasonic velocity values. In addition,

other available hypersonic velocity data²³ at 5 GHz, extended in the supercooled region down to -20 °C, show a monotonic decrease. Although in our previous measurements²⁰ the temperature range explored was lowered down to -27 °C, showing the above described minimum, we were unable to perform a definite choice between the two conjectures (relaxation phenomena or thermodynamic anomaly due to heterophase fluctuations). Because we have also shown that the latter hypothesis is ultimately reduced again to a relaxation process, we have evaluated the strength and the mean relaxation time. The value of this latter was of the order of 10 ps (16 ps if the relaxation is only structural in character, 8.5 ps if the relaxation is structural and viscous) at the temperature of -27 °C. As one can fully understand the microscopic process only if the acoustic parameters are analyzed as a function of the frequency, we anticipated in that work "a series of Brillouin measurements as a function of the exchanged momentum...will allow a better insight into the controversial problem of the supercooled water". The occurrence of a relaxation phenomenon was later²⁴ supported by studying the temperature evolution of the ratio between the central and the shifted doublet intensities (the Landau-Placzek ratio R_{L-P}). The R_{L-P} values, in fact ($\sim 10^{-3}$ at 10 °C), show a monotonic increase of about 2 orders of magnitude when the temperature of -26 °C is reached. This indicates that a considerable redistribution of the spectral intensity occurs between the Brillouin lines and the nonshifted term and it is due to the addition of the isobaric entropy fluctuation term (Rayleigh) to the diffusive portion of the adiabatic pressure fluctuations (Mountain mode). As a matter of fact, the anomalous increase of the R_{L-P} in the supercooled region was rationalized by inserting in the R_{L-P} calculation (i) the observed ω dependence of the elastic coefficient (i.e., the adiabatic compressibility β_s , evaluated at $\omega = 5$ GHz) and (ii) an explicit temperature dependence of the dielectric constant derivatives $(\partial\epsilon/\partial\rho)_T$ and $(\partial\epsilon/\partial T)_\rho$. The nonzero value of this latter quantity suggested that the relaxation process could be structural in character. The hypothesis that the relaxing structural entities are connected to the extended correlated regions (polyhedra?) in supercooled water was supported by the temperature dependence of the T derivative of $(\partial\rho_1/\partial T)_\rho$, where ρ_1 is the number density of the structured water molecules contributing to the R_{L-P} via the dielectric constant. In fact, Figure 6 of ref 24 shows that the more complex the structure is, the more rapidly the T derivative of the corresponding concentration number increases when T decreases. Since the slope of $(\partial\rho_1/\partial T)_\rho$ vs T is higher than the corresponding derivative for pentagonal units,²⁵ we supposed that the observed relaxational phenomena was connected with a super arrangement of pentagonal units in polyhedra.

An immediate way to give reasons for the supposed relaxation process in water is, as written before, the study of the ω -dependent hyperacoustic velocity and absorption. With this in mind we have performed a careful analysis of the hydrodynamic triplet by a Mandelstam-Brillouin scattering experiment. The measurements, carried out for the first time as a function of the exchanged momentum k in bulky water, down to -27 °C, allows us to confirm the presence of an acoustic relaxation phenomenon. We will show that, due to the high degree of cooperation in the dynamical properties of our system, a dissipative bulk and/or shear phenomenon that is ω and T dependent is observed. A similar behavior has been reported in literature for moderately supercooled liquids²⁶⁻²⁸ with a high degree of intermolecular coupling effects. From the ω -dependent velocity and absorption data, the relaxing modulus and the relaxation time will be calculated in the framework of existing viscoelastic theories^{28,29} and discussed on

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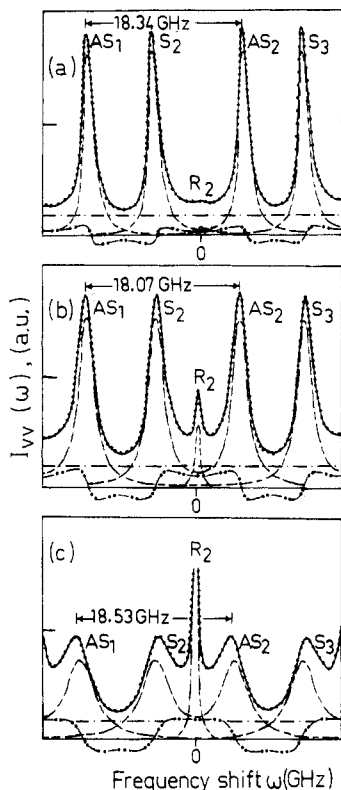


Figure 1. Mandelstam-Brillouin spectra in water at 90° of scattering angle and at different temperatures: (a) $T = -0.4$ °C, FSR (free spectral range) = 18.34 GHz; (b) $T = -15.4$ °C, FSR = 18.07 GHz; (c) $T = -27.4$ °C, FSR = 18.53 GHz. S and AS refer to Stokes and anti-Stokes components, respectively; R refers to the central component. Points: experimental data (—); theoretical fitting by eq 2; (---) Rayleigh component; (-.-) symmetric Brillouin components; (·-·) asymmetric Brillouin components; (···) flat background.

the basis of new experimental and theoretical results in supercooled water.

Experimental Procedure and Data Analysis

Polarized Brillouin spectra were performed in the 20 to -27 °C temperature range in high-purity liquid water purchased in a 10-cm³ volume vial from the Angelini pharmaceutical industry. The sample was selected from a large number of vials, to obtain the quasi-total absence of stray light (tested by performing preliminary optical measurements at room temperature) and the lowest supercooling limit. To avoid any contamination, we put the sealed vial into an especially built optical thermostat. The temperature stability was better than 0.02 °C over the temperature range investigated. Brillouin scattering measurements were performed by a Tropel Model 350 plane piezoelectrically scanned Fabry-Perot interferometer that was driven by a microcomputer. The scattered intensity collected by a thermoelectrically cooled PM Model RCA c-31034 (dark photon counts fewer than 10 counts/s) was normalized by the incident intensity and stored by the same microcomputer. We used the 4880-Å line of a unimode Ar⁺ laser (Spectra-Physics Model 170) working at a mean power of 500 mW as our exciting source.

The polarized Brillouin spectra were taken at the four scattering angles 30°, 60°, 90°, and 150°. The free spectral range (FSR) of the Fabry-Perot interferometer was chosen with a range between ~7.5 and ~18.5 GHz, to have the best compromise between the thermal phonon doublet shift and the resolution. The obtained mean overall finesse of the interferometer was 45. The transferred wavevector values $k = (4\pi/\lambda)n(T) \sin \theta/2$ ranged from $\sim 8.9 \times 10^4$ cm⁻¹ at -27.4 °C and the scattering angle of 30° to $\sim 33.1 \times 10^4$ cm⁻¹ at -27.4 °C and the scattering angle of 150°. In this way, the frequency range between ~1.7 and ~8 GHz was

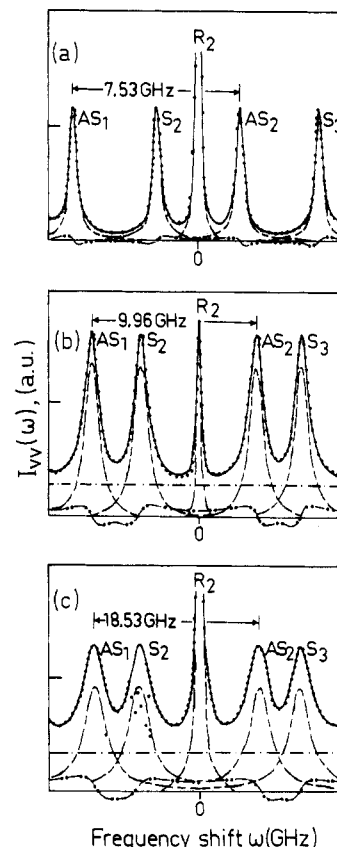


Figure 2. Mandelstam-Brillouin spectra in water at various scattering angles θ and different temperatures T : (a) $\theta = 30^\circ$, $T = -10.8$ °C, FSR = 7.53 GHz; (b) $\theta = 60^\circ$, $T = -15.2$ °C, FSR = 9.96 GHz; (c) $\theta = 150^\circ$, $T = -15.0$ °C, FSR = 18.53 GHz. The other symbols are coincident with those of Figure 1.

spanned. Finally, many spectra were taken at each temperature and then properly added to increase the photon statistics. In such a way we obtain a good data reproducibility with a high signal-to-noise ratio. The estimated overall error in determining hypersound velocity and absorption was lower than 1% for the former and lower than 2% for the latter. The auxiliary data, necessary to evaluate the acoustic quantities of interest, concerning the density ρ and the refractive index n at the various temperatures, were taken from literature.^{30,31} In Figure 1 we show, as an example, three typical Brillouin spectra in liquid water taken at 90° of the scattering angle at the temperatures of -0.4 (a), -15.4 (b), and -27.3 °C (c) and their theoretical fits (see below). Furthermore, in Figure 2 examples are reported of Brillouin spectra that refer to $T = -10.8$ °C and $\theta = 30^\circ$ (a), to $T = -15.2$ °C and $\theta = 60^\circ$ (b), and to $T = -15.0$ °C and $\theta = 150^\circ$ (c) showing the angular dependence of the various spectral features by the scattering angle θ . As far as the analysis of the Brillouin spectra is concerned, the hydrodynamic equations allow us to understand the spectral behavior of moderately supercooling liquids (MLS) such as water quite well. The fully polarized scattered intensity measured, which in a light-scattering process is proportional to the double-differential cross section, furnishes direct information about the dynamical structure factor $S(k, \omega)$ of the system. This quantity, defined as the Fourier transform of the k th component of the time fluctuations correlation function of the pressure and temperature-induced density $C_p(k, \omega) = \langle \delta \rho^*(k, 0) \cdot \delta \rho(k, t) \rangle$ is given by

$$S(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} C_p(k, t) \quad (1)$$

Following the Boon and Yip²⁷ formalism, it is possible to calculate

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$C_p(k, t)$ and hence $S(k, \omega)$, which in the case of moderately viscous liquids becomes

$$S(k, \omega) = \frac{1}{\pi} V \rho_0^2 K_B T \beta_T \left\{ \frac{1-\gamma}{\gamma} \frac{2D_T k^2}{\omega^2 + (D_T k^2)^2} + \frac{1}{\gamma} \left(\left[\frac{\Gamma_B(k)}{[\omega - (\omega_0^2 - \Gamma_B^2(k))^{1/2}]^2 + \Gamma_B^2(k)} + \frac{\Gamma_B(k)}{[\omega + (\omega_0^2 - \Gamma_B^2(k))^{1/2}]^2 + \Gamma_B^2(k)} \right] + \frac{\Gamma_B(k)}{(\omega_0^2 - \Gamma_B^2(k))^{1/2}} \left(\frac{\omega + [\omega_0^2 - \Gamma_B^2(k)]^{1/2}}{[\omega + (\omega_0^2 - \Gamma_B^2(k))^{1/2}]^2 + \Gamma_B^2(k)} - \frac{\omega - [\omega_0^2 - \Gamma_B^2(k)]^{1/2}}{[\omega - (\omega_0^2 - \Gamma_B^2(k))^{1/2}]^2 + \Gamma_B^2(k)} \right) \right\} \quad (2)$$

where the symbols have the usual meaning. Equation 2 yields the shape of the Mandelstam-Brillouin spectrum from an MSL. The first term in the braces takes into account the isobaric fluctuations and is diffusive in character. The second term takes into account the existence of adiabatic pressure fluctuations (thermal phonons) in the system. This doublet refers to creation (Stokes) and annihilation (anti-Stokes) events in the scattering process and is symmetric in character. The third term is a manifestation of the sum rule for the first moment $(1/2\pi) \cdot \int_{-\infty}^{+\infty} S(k, \omega) \omega d\omega = 0$ ²⁷ and was historically evaluated by Litovitz et al.³² This term has the usual doublet structure, is shifted in frequency, is asymmetric, and does not give rise to any contribution by integrating it over ω . It is to be noted that if the system shows a relaxation process, eq 2 becomes more complex. In such a case, in fact, the transport coefficients that enter eq 2, i.e., the thermal diffusivity and the bulk and shear viscosities, are substituted by the generalized transport functions.²⁷ The most spectacular manifestation of the dispersive character of the transport coefficients is the presence of new spectral features (the Mountain mode) that arise from a nonoscillatory adiabatic pressure fluctuations and lie in the central region of the spectrum.^{32,33} We have shown in the General Considerations that this contribution induces the anomalous increase of the R_{L-P} in supercooled water. Nevertheless, because the structure of the scattering equation is similar to that of eq 2 and since we are here analyzing only the shifted spectral components, we have fitted the experimental spectra with eq 2 to subsequently test the ω dependence of the acoustic parameter. In particular, the true line width was obtained by deconvolution with the instrumental resolution function (IRF). The IRF of our interferometer was evaluated for each FSR by the measured spectra of a latex aqueous suspension. The results of the fitting by eq 2 are represented by solid lines in Figures 1 and 2 with the experimental points (dots). The probe-independent frequency shift ω_0 and the line width Γ_B were evaluated, and finally the hypersonic velocity $v_s = \omega_0((4\pi/\lambda)n \sin \theta/2)^{-1}$ and the absorption $\alpha/f^2 = 2\pi\Gamma_B/(v_s\omega_0^2)$ were calculated as a function of the temperature T and of the scattering angle θ (and hence of the frequency ω).

Discussion

The temperature and frequency dependence of the sound velocity v_s in supercooled water is shown in Figure 3. It clearly appears that the sound speed data are strongly θ dependent when the temperature is lowered to $\sim -15^\circ\text{C}$. The sound speed data at the lower angle of 30° (corresponding to an ω_0 value of ~ 1.27 GHz at $T = -27.4^\circ\text{C}$), in the figure, show a monotonic decrease at lower temperatures and, in the temperature range explored, practically coincide with those of Trinh and Apfel²¹ (full circles in the figure) taken at 54 kHz. At the higher scattering angles,

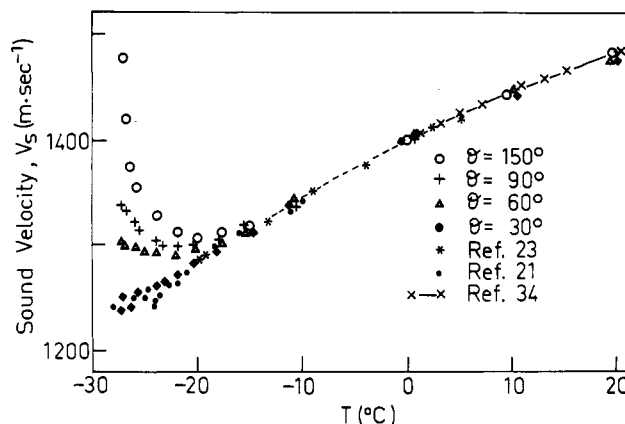


Figure 3. Temperature evolution of the sound velocity v_s at different scattering angles θ . \circ , $+$, Δ , and \diamond are our results; \bullet , ref 21; $*$, ref 23; \times , ref 34.

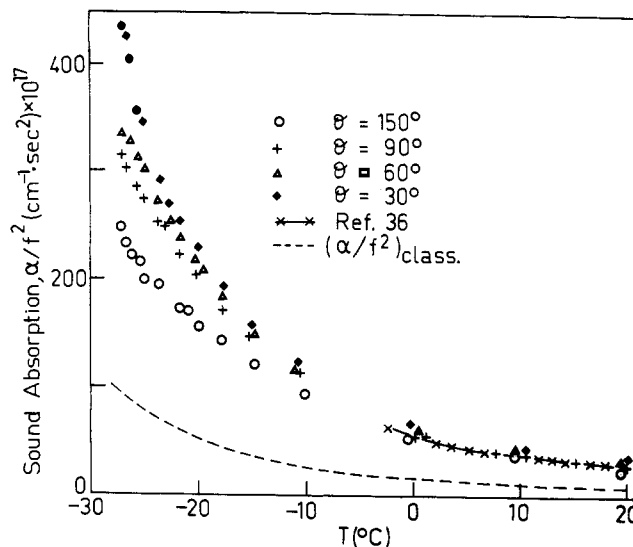


Figure 4. Temperature evolution of the sound absorption α/f^2 , at different scattering angles θ . \circ , $+$, Δ , and \diamond are our results; \times , ref 36; (---) $(\alpha/f^2)_{\text{class}}$.

we can observe a systematic increase of the velocity in the deeply supercooled region, with a well-defined minimum shifting toward higher temperatures when θ increases. Furthermore, it is to be noted that the ultrasonic data of ref 21 tend to flatten at temperatures lower than -30°C , thus so indicating, in agreement with our observation, that the minimum shifts toward lower temperatures at lower frequencies. Finally the 150° data, which correspond to a frequency of ~ 8 GHz (open circles in Figure 3), show the largest effect. In the same figure, other available sound speed data are also reported such as Brillouin data²³ taken at ~ 5 GHz and extending down to -20°C (asterisk in the figure) and ultrasonic data by Del Grosso and Mader³⁴ in the normal liquid region (crosses and solid line in the figure). The most striking phenomenon that we observe at low temperatures, i.e., the minimum in the velocity data, can be connected to the zero-frequency adiabatic compressibility increase^{24,35} onto which a relaxational (ω dependent) effect of the longitudinal modulus is superimposed. The propagating density fluctuations (i.e., elastic waves at a velocity v_s) are damped by shear and bulk viscosity and heat conduction within the medium. These quantities contribute to the high-frequency acoustic absorption α/f^2 , whose temperature dependence is shown in Figure 4. As can be seen, a typical relaxational behavior is quite evident: the data, nearly frequency independent in the temperature range from 20 to -10°C , flatten noticeably in the deeply supercooled region, going from the lowest

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scattering angle to the highest one. In particular, when the lowest temperature values at 30° (rhombuses in the figure) and at 150 °C (open circles) of scattering angles are compared, a hypersound absorption decrease of about a factor 2 is observed. In the same figure the ultrasonic data³⁶ (crosses and line) in the normal liquid region and the classical absorption due to the shear viscosity are also shown.

The observed relaxational phenomenon has a microscopic origin because of the nonzero time value necessary for the restoring forces to drive the system to a local equilibrium altered by the local pressure fluctuations. This phenomenon, which we have used to explain the temperature behavior of our previous Rayleigh-Brillouin data, has been confirmed by Clementi and Wojcik¹⁶ (C-W). In their impressive work, by taking into account two- and three-body forces, they show that a positive dispersion in the sound velocity exists in water. Using generalized hydrodynamics and analyzing the $S(k, \omega)/S(k)$ factor (i.e., the normalized dynamic structure factor) for $0.25 \leq k \leq 0.6 \text{ \AA}^{-1}$, C-W were able to extract the sound velocities $v_0(k)$, $v_s(k)$, and $v_\infty(k)$ for two- and three-body liquid water at room temperature, furnishing a rather convincing theoretical suggestion that dispersive phenomena take place in water. The origin of the collective mode dispersion, recently discovered by Teixeira et al.³⁷ in a coherent inelastic neutron-scattering (CINS) experiment in heavy water at room temperature, has been explained on the basis of a relaxation phenomenon connected with¹⁶ "the strength of the longer ranged attractive forces in the intermolecular potential". By returning now to our results, the experimentally discovered positive dispersion in the deeply supercooled water resembles the positive dispersion observed by C-W in simulated water. Therefore, considering that for spontaneous scattering processes in moderately supercooled liquids (as water is) the linear viscoelastic theory holds, we can derive some expressions for the complex longitudinal modulus^{27-29,38} \tilde{M} whose real part M' (the storage modulus) is connected with the sound speed while its imaginary part M'' (the loss modulus) is related to the sound absorption. Generally, in associated supercooled liquids the relaxation processes take place with an appropriate distribution function $f(\tau)$. In such a case the complex modulus \tilde{M} becomes

$$\tilde{M} = \tilde{M}_0 - (\tilde{M}_\infty - \tilde{M}_0) \int_0^\infty f(\tau) \frac{i\omega\tau}{1 - i\omega\tau} d\tau \quad (3)$$

The integral in (3) is substituted by a sum over n steps, if n separated relaxational events occur in the system. A more simplified assumption is that the relaxation processes are well decoupled into separate steps and that, for each step, the distribution $f(\tau)$ is "narrow". In such a case, the relaxation time of each step can be considered as a mean value. Under this assumption, one can write

$$\tilde{M} = M' + iM'' =$$

$$K_r^{\text{str}} \frac{\omega^2 \tau_v^2}{1 + \omega^2 \tau_v^2} + i\omega\eta_v(\omega) + \frac{4}{3}G_\infty \frac{\omega^2 \tau_s^2}{1 + \omega^2 \tau_s^2} + i\frac{4}{3}\omega\eta_s(\omega) \quad (4)$$

In (4) K_r^{str} is the relaxing compressional modulus, G_∞ is the shear modulus, and τ_v and τ_s are respectively the structural and the shear relaxation times. Since in supercooled water relaxation processes different from those represented above (such as chemical, vibrational, etc.) are unlikely to occur, we have applied eq 4 to our data, obtaining

$$v_s^2(\omega, T) = \frac{1}{\rho(T)} \left[K_0(T) + K_r^{\text{str}}(T) \frac{\omega^2 \tau_v^2(T)}{1 + \omega^2 \tau_v^2(T)} \right] \quad (5)$$

$$\frac{\alpha(\omega, T)}{f^2} = \frac{2\pi^2}{\rho(T)v_s^3} \left[K_r^{\text{str}}(T) \frac{\tau_v(T)}{1 + \omega^2 \tau_v^2(T)} + \frac{4}{3}\eta_s(T) \right] \quad (6)$$

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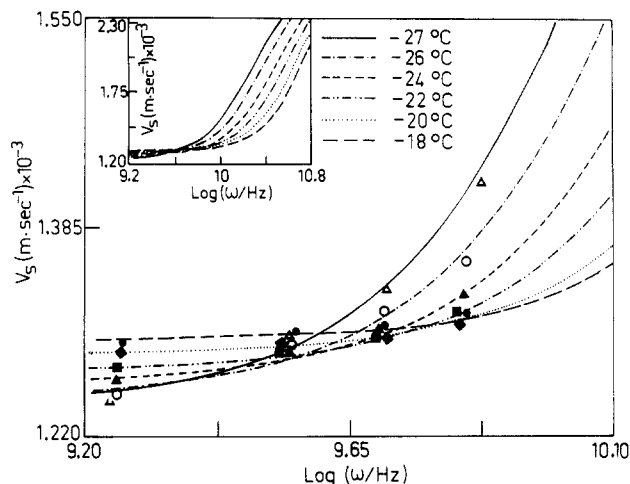


Figure 5. Hypersonic velocity v_s vs frequency ω at various temperatures T . ●, ◆, ■, ▲, ○, and △ are our results. The different lines refer to the velocity calculated by eq 5. In the inset the theoretical values are shown on a more enlarged scale.

by hypothesizing that only a structural relaxation process is occurring. In the case of simultaneous relaxations of "structural" and "shear" processes, we can write

$$v_s^2(\omega, T) = v_{s,0}^2(\omega, T) + \frac{1}{\rho(T)} \frac{M_r(T) \omega^2 \tau^2(T)}{1 + \omega^2 \tau^2(T)} \quad (7)$$

$$\frac{\alpha(\omega, T)}{f^2} = \frac{2\pi^2}{\rho(T)v_s^3} \frac{M_r(T) \tau(T)}{1 + \omega^2 \tau^2(T)} \quad (8)$$

Equations 5 and 6, provided that the zero-frequency value of the compressional modulus $K_0 = \rho v_{s,0}^2$ is known, yield the values of the relaxing compressional modulus K_r^{str} and of the bulk relaxation time τ_v , where $\omega\tau_s \ll 1$, i.e., the shear viscosity is not relaxing. Equations 7 and 8 give the values of the relaxing shear modulus $M_r = K_r^{\text{str}} + \frac{4}{3}G_\infty$ and of the relaxation time τ , when $\tau = \tau_s = \tau_v$. It is to be noted that because of the lack of complementary information about this relaxation process in the supercooled region, we are unable to perform a definite choice between the two sets of equations. In addition, an inspection of Figures 3 and 4 shows that we are in a limited $\omega\tau$ region. The impossibility of obtaining data in a more extended range of temperature in the supercooled region (even if the value of -27.4 °C reached in our experiment in bulk samples can be considered unusual) added to the lack of data at higher frequency values, did not allow us to perform a detailed analysis of the relaxation process involved. Being aware that some criticism could be raised against the assumption that structural and/or shear processes in supercooled water follow a simple exponential time decay, we used both the two sets of equations for the fit procedures. Figure 5 shows, as an example, the frequency dependence of the sound speed in a semilog plot for temperatures ranging from -18 to -27 °C. The various lines in the figure are the theoretical curves obtained from eq 5. In the inset of Figure 5, the same theoretical curves are represented on a more enlarged scale, so that some detail about the relaxation process can be shown. Figure 6 shows the fit of the sound speed data by eq 7. The inset shows the theoretical evolution of this structural plus shear relaxation governed by a single rate process. From the velocity data fitting procedure we obtained the values of τ_v and K_r^{str} , under the hypothesis that $\tau_v \gg \tau_s$, and the values of τ and M_r , under the hypothesis that $\tau_v = \tau_s = \tau$. In the first case it turns out that τ_v ranges from 2.3 to 9.4 ps and K_r ranges between 4.9×10^{10} and $2.6 \times 10^{10} \text{ dyn/cm}^2$ in the temperature range -18 °C $\geq T \geq$ -27 °C. Under the second hypothesis, τ ranges from 1.6 to 6.5 ps and M_r ranges from 10.1×10^{10} to $5.5 \times 10^{10} \text{ dyn/cm}^2$ in the same temperature range.

If an analogous best fit for the sound absorption data is performed by eq 6 and 8, the same relaxation times are obtained, whereas the relaxation strengths K_r and M_r show some discordance compared with the corresponding values from the sound speed

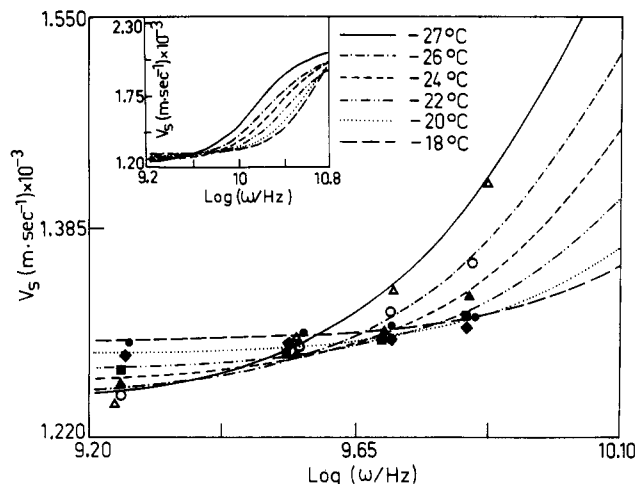


Figure 6. Hypersonic velocity v_s vs frequency ω at various temperatures T . ●, ■, ▲, ○, and △ are our results. The different lines refer to the velocity calculated by eq 7. In the inset the theoretical values are shown on a more enlarged scale.

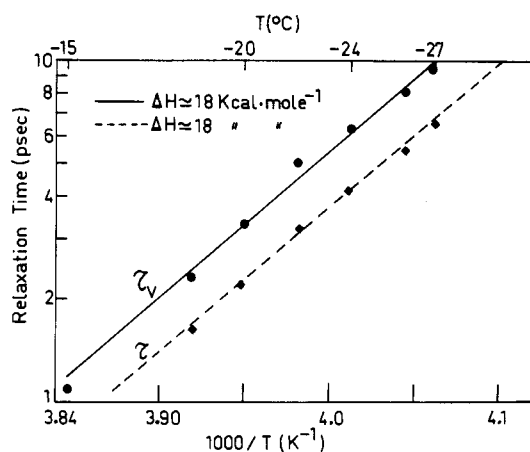


Figure 7. Arrhenius fit of the mean relaxation times. ● and ◆ are the experimental data for structural (τ_v) and structural plus shear (τ) relaxation times, respectively.

data. In our opinion, this fact indicates that single relaxation models are too crude an approximation for water. Moreover, to furnish information about the acoustic dispersion that is shown in this experiment, we look at the temperature evolution of the relaxation time. From the plot of $\ln \tau$ vs $1/T$ it is possible to obtain the "mean activation energy" of the process. The results are shown in Figure 7, where the Arrhenius fit for both τ_v and τ furnishes the same "mean activation enthalpy" of ~ 18 kcal mol $^{-1}$. This value seems to be overestimated respect to other results in water.^{1,2} Such a circumstance reinforces the idea that a more complex relaxation mechanism holds in supercooled water. As a matter of fact, by considering that the ratio τ_s/τ_v in the C-W simulated water is about 1.3, under the hypothesis that such a value is maintained in real water at subzero temperatures, we can expect the following: (i) The relaxation time values are not too affected by the presence of two nearly but not exactly coincident relaxation processes. In such a case our τ data can be considered as mean values. (ii) The relaxation strengths, which enter the sound speed and absorption formula^{28,38} in a different way, can largely differ from our estimated values. In such a case the above observed

inconsistency could be removed. (iii) If many (at least two) steps take place in the relaxation process, our calculated backward barrier height could be considered as the sum of the different enthalpy values through which the system evolves.

As far as the sound velocity $v_{s,\infty}$ extrapolated to infinity frequency is concerned, its values at the temperature of -27 °C are ~ 2100 and ~ 3000 m/s for structural and structural plus shear relaxation processes, respectively. These values, which correspond to the sound speed of purely elastic propagating waves in supercooled water, are of the same order of magnitude as the $v_{s,\infty}$ data obtained by C-W in their simulated water, when these latter values are reduced to our temperature.

Concluding Remarks

In this paper we have presented new experimental results concerning the sound speed and the relative damping parameter in deeply supercooled water. The main results obtained can be summarized in the following points:

The Mandelstam-Brillouin spectra obtained in H₂O down to -27.4 °C as a function of temperature T and of the scattering angle θ show a behavior quite similar to that observed in other moderately supercooled liquids. Since the associative properties of liquid water are more enhanced at subzero temperatures, where the viscosity increases, a viscoelastic behavior appears in the transport coefficients. Consequently, as we have shown the relevant quantities ω_0 and Γ and hence v_s and α/f^2 become ω dependent in the temperature region -18 to -27.4 °C, in the frequency range from ~ 1.2 to ~ 8 GHz.

The tendency of the sound speed to flatten when T reaches ~ -23 °C, which was anticipated in a previous work,²⁰ is definitely confirmed. Furthermore, as expected in a dispersive region,²⁸ the velocity minimum shifts to higher temperatures when the frequency increases.

The sound absorption tends to its classical value when it is deeply supercooled. This effect also increases with ω .

The reduced $\omega\tau$ range investigated allows us to apply only a simplified viscoelastic model. The relaxation strength and the relaxing time values are also extracted and discussed. The latter quantity shows an Arrhenius behavior for both the hypotheses that only a structural or a structural plus a shear relaxation phenomenon takes place. The value of the activation enthalpy we obtain (~ 18 kcal mol $^{-1}$) is overestimated compared to other backward energy barriers in supercooled water, evaluated by the T dependence of other quantities.^{1,2,6} This fact can also be connected to the limitation of the simple applied model. As a matter of fact, if simultaneous relaxations of bulk and shear viscosity occur, with small different relaxation times τ_v and τ_s , a lower value of the activation enthalpy is to be expected.

The extrapolated high-frequency elastic speed $v_{s,\infty}$ for $T = -27$ °C has a value of ~ 2100 m/s if $\tau_s \ll \tau_v$ and of ~ 3000 m/s if a structural plus shear relaxation takes place.

This latter value recalls the one obtained by Clementi and Wojcik¹⁶ in their simulated three-body water.

As far as the physical origin of our observed hypersound dispersion is concerned, it is certainly connected with the extended network, built up in the supercooled region around the H-bond imposed tetrahedral local arrangement. On the other hand, the indication that many-body collective effects take place in supercooled water is a manifestation that long-range terms are to be accounted for the intermolecular potential.¹⁶ To give more information about the dispersive phenomena in supercooled water presented in this paper, new scattering experiments are planned.

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