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Analysis of the dispersion of the sound velocity in supercooled water

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Résumé. — La vitesse du son dans l'eau a été mesurée aux fréquences ultrasonores et hypersonores et les résultats mettent en évidence une dispersion négative dans la région de surfusion. Nous présentons des mesures de vitesse du son et d'absorption obtenues par diffusion de la lumière (diffusion Brillouin) qui montrent que l'effet de relaxation structurale n'est pas observé à 0 °C et aux fréquences inférieures à 7,2 GHz. Une correction des données hypersonores montre qu'il n'apparaît aucun désaccord entre les données ultrasonores et hypersonores.

Abstract. — The sound velocity in water has been measured at ultrasonic and hypersonic frequencies and the results show a negative dispersion in the supercooled region. We present measurements of sound velocity and absorption obtained by Brillouin light scattering which show that the effect of structural relaxation is not observed at 0 °C and frequencies smaller than 7.2 GHz. A correction of the hypersonic data shows that there is no apparent disagreement between the ultrasonic and the hypersonic data.

1. **Introduction.** — Supercooled water has been intensively studied in recent years. Both the thermodynamic and the transport properties show an anomalous temperature dependence which suggests a singularity at − 45 °C [1]. The sound velocity has been measured by several groups using both ultrasonic [2, 3] and light scattering [4, 5] techniques. The results show a negative dispersion, i.e. a sound velocity at high frequencies slightly smaller than the sound velocity at low frequencies. We have now both ultrasonic and hypersonic data in a common temperature range extending down to − 20 °C and it is possible to compare the different results. We intend in this paper to show that the observed dispersion can be explained if one takes into account rigorously the peculiarities of the two techniques used. We shall discuss also the interpretations given elsewhere [3, 4, 6] for this problem.

It is well known from the classical theory of sound propagation that an excess ultrasonic absorption appears in a liquid as a result of the molecular rearrangements during the acoustic compression.

The compressibility β has then an imaginary part and can be written, if one uses the Maxwell model, as $\beta - \beta_\infty = \beta_r/(1 + i\omega\tau)$ where $\beta_r \equiv \beta_0 - \beta_\infty$ is the difference between the zero and the infinite frequency compressibilities and τ is the structural relaxation time. The consequence for the sound velocity is a positive dispersion which can be described in first approximation by the following expression :

$$v^2 - c_0^2 = (c_\infty^2 - c_0^2)\frac{\omega^2\tau^2}{1 + \omega^2\tau^2} \qquad (1)$$

where v is the sound velocity at frequency $f = \omega/2\pi$ and c_0 and c_∞ are the sound velocities at zero and infinite frequency respectively.

When the influence of the structural relaxation time is negligible, i.e. $\omega\tau \ll 1$, and if the thermal diffusivity is also negligible, the dispersion equation is [7] :

$$-\omega^2 + i\omega b k^2 + c_0^2 k^2 = 0$$

where k is the wave vector and

$$b \equiv \frac{1}{\rho_0}\left(\frac{4}{3}\eta_s + \eta_B\right)$$

takes in account the absorption which results from both the shear, η_s, and the bulk, η_B, viscosities. ρ_0 is the density of the liquid.

In a light scattering experiment, the wave vector k is imposed and, consequently, it is a real number. From equation (1) one obtains :

$$i\omega = -\frac{1}{2}bk^2 \pm ic_0 k\left(1 - \frac{b^2k^2}{4c_0^2}\right)^{1/2}$$

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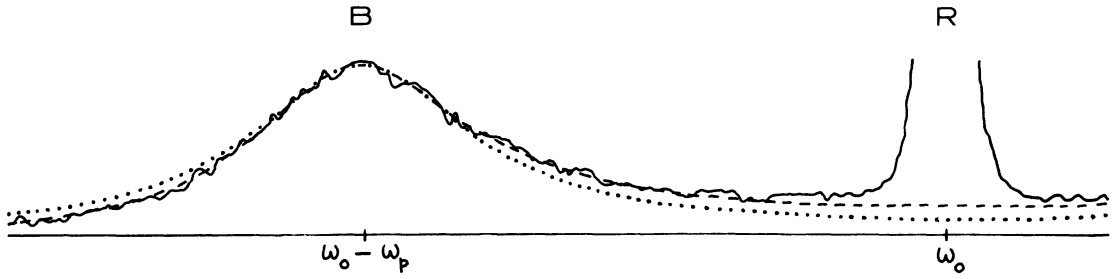

Fig. 1. — Rayleigh (R)-Brillouin (B) spectrum at $T = -20.2$ °C. --- Theoretical spectrum deduced from the hydrodynamic equations in the case of a non-relaxing liquid : $\omega_p \simeq \omega_B \left(1 - \frac{1}{2}\frac{\Gamma_B^2}{\omega_B^2}\right)$; ... Theoretical spectrum obtained neglecting the asymmetric contribution to the Brillouin line : $\omega_p = \omega_B$.

then, the velocity of phase is

$$v_B = c_0 \left(1 - \frac{b^2 k^2}{4 c_0^2}\right)^{1/2} \tag{2}$$

where

$$\Gamma_B = \frac{bk^2}{2}$$

is the half-width of Brillouin lines and $\omega_B = k v_B$ is the Brillouin line shift.

Because the Brillouin lines are asymmetric (see Fig. 1), the frequency ω_B is different from the value, ω_p, measured on the spectrum between the Brillouin peaks and the central line. The ratio between these two quantities is [8] :

$$\frac{\omega_B}{\omega_p} \simeq 1 + \frac{1}{2}\frac{\Gamma_B^2}{\omega_B^2}. \tag{3}$$

Equation (2) together with equation (3) give for the zero frequency sound velocity

$$c_0 \simeq \frac{\omega_p}{k}\left(1 + \frac{\Gamma_B^2}{\omega_p^2}\right). \tag{4}$$

To compare the results obtained in light scattering and ultrasonic experiments a preliminary correction using equation (4) has to be made.

In the next section, we show the results obtained after applying equation (4). Moreover, in order to prove that the structural relaxation can be neglected, we compare the results obtained for sound velocity and absorption at 0 °C, at two relatively high frequencies : 5 and 7.2 GHz, obtained with the same technique.

2. **Experimental results and discussion.** — In figure 2, the results obtained for the sound velocity in ultrasonic measurements by Trinh and Apfel [2] at $f = 3$ MHz are presented together with the results in a light scattering experiment, using a capillary as previously described [5]. The velocity v is obtained there, from the Brillouin lines shift, ω_B, using the expression :

$$v = \frac{\omega_B \lambda}{2\pi n} \frac{1}{2 \sin \frac{\theta}{2}}$$

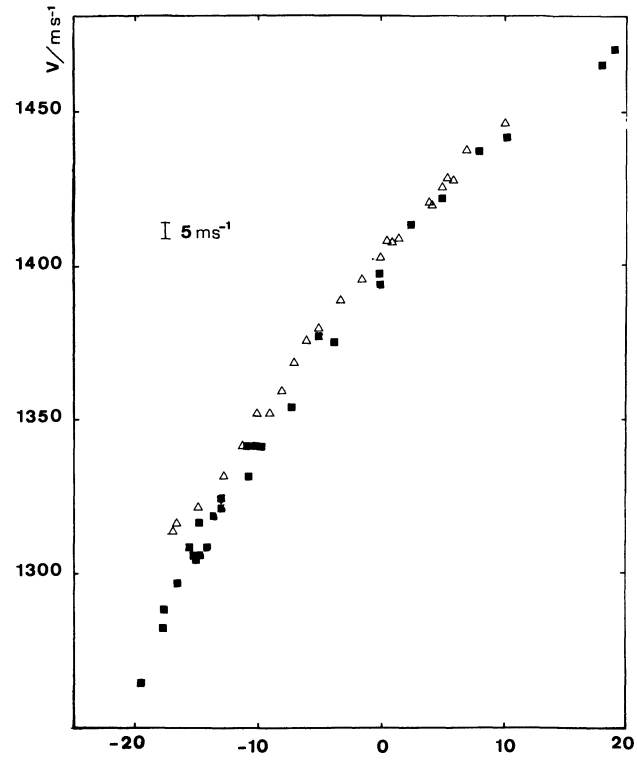

Fig. 2. — Variation of the sound velocity, v, with the temperature T. Full squares : hypersonic [5] ; triangles : ultrasonic [2].

where $\theta = 90°$ is the scattering angle, λ the wavelength of the laser light and n the refractive index of water. This calculation supposes $\omega_p = \omega_B$.

It is clear from figure 2 that a negative dispersion appears at low temperatures and that, at -15 °C, it is as big as 1 %. However, in order to compare the two sets of results, we use the theory described in the preceding section.

The first question concerns the structural relaxation. Actually, we test if the assumption $\omega\tau \ll 1$ is verified in all the measured frequency range.

In water, the correlation time for molecular reorientation has been measured by different techniques [9-11] and the results agree for a value of 5 ps at 0 °C. The temperature dependence of this characteristic time is well described by a critical law [12]. At -20 °C, it should reach a value as high as 15 ps.

On the other hand, the model usually accepted for the molecular motions in water supposes a *jump and wait* mechanism [13]. The molecules stay for a time τ_0 in a site and jump during a time τ_1 to a new site. τ_1 is much smaller than τ_0, which is measured in dielectric relaxation [9] and NMR experiments [10]. For τ_1, the experimental results are less clear, but from neutron scattering [14] and depolarized light scattering [11], one can predict a value of the order of 1 ps. τ_1 is probably not *critical*, i.e. its temperature dependence is Arrhenius-type, which gives at -20 °C a value for τ_1 only slightly larger than 1 ps.

It is difficult to predict the exact mechanisms of the structural relaxation in water and different approaches have been made [13, 15]. The answer is important for the discussion of the possible positive dispersion of the sound velocity, because the assumption $\omega\tau \ll 1$ at $f = 5$ GHz is not adequate if $\tau > 5$ ps.

To evaluate the order of magnitude of $\omega\tau$, we carried out two Brillouin light scattering experiments under exactly the same conditions (sample, laser power, and wavelength, detection system, temperature) and at two different scattering angles θ. This enables us to obtain the sound velocity and absorption at the two frequencies 5 and 7.2 GHz and compare the results independently of parameters other than the frequency.

We used a cell containing 5 cm^3 of doubly-distilled, deionized and filtered water at a temperature equal to 0° $\pm$ 0.01 °C. The light is provided by a Ar^+ laser and the wavelength is $\lambda = 514.5$ nm. We measured the spectrum of scattered light for $\theta = 90°$ and $\theta = 170°$. The results are given in table I.

The conclusion is that, below 7.2 GHz, we do not see any relaxation effect in either the sound velocity or the absorption, because either the structural relaxation time, or the term $(c_\infty^2 - c_0^2)$ in expression (1) is too small. This result disagrees with the experiment of Bacri and Rajaonarison [3], who find an important dispersion in the absorption. The explanation of their results remains unclear especially as it is not accompanied by any dispersion of the sound velocity.

We can use the theory developed on section 1 to correct the hypersonic sound velocity data using equation (4) in order to compare them with the ultrasonic data. The result is shown in figure 3. It is clear that, within the experimental error, the two sets of data agree quite well.

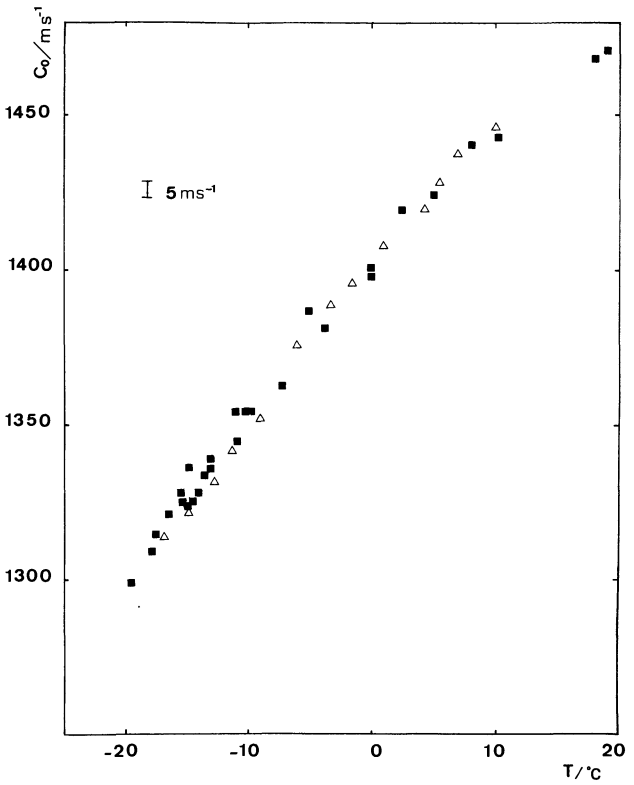

Fig. 3. — Comparison between the ultrasonic data for sound velocity (triangles) and the hypersonic data (full squares) corrected by equation (4).

3. **Conclusion.** — The apparent discrepancies between ultrasonic and hypersonic sound velocity can be understood if the calculation of the zero-frequency sound velocity is made correctly. Consequently, it seems that the isentropic conditions are well verified in both ultrasonic and hypersonic experiments. This should not be perhaps the case if the experiments are done at lower frequencies, say in the kHz range. Under such conditions, the interpretation of Leyendekkers [6] could apply.

On the other hand, we have concluded, from our measurements of sound velocity and absorption that the effects of structural relaxation cannot be seen above -20 °C. It would be interesting to extend the measurements to lower temperatures in order to investigate these effects and to deduce the structural relaxation mechanism in water.

Table I. — *Velocity of sound, v, and absorption, α/f^2 at temperature $T = 0$ °C and frequency f.*

Scattering angle θ	Frequency f/GHz	Sound velocity v/m.s^{-1}	Zero-frequency sound velocity c_0/m.s^{-1}	Absorption $10^{14} \cdot \frac{\alpha}{f^2}$/m^{-1}.s^2
—	—	—	—	—
90°	5.135	1 401 $\pm$ 7	1 404 $\pm$ 7	4.3 $\pm$ 0.4
170°	7.235	1 392 $\pm$ 7	1 400 $\pm$ 7	4.6 $\pm$ 0.4

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