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Hyperacoustic velocity of fluid hydrogen at high pressure

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Abstract. The hypersonic velocity has been measured in fluid hydrogen at room temperature in the pressure range 60 MPa–5 GPa, by means of Brillouin light scattering in a large-volume optical gas cell and in a diamond anvil cell. These new data are compared with previous Brillouin results and with acoustic measurements, existing up to 2 GPa, to discuss dispersion of sound in high-pressure fluids. An accurate functional form for the fluid density as a function of pressure above 2 GPa has been derived from the present Brillouin results.

The description of acoustic-like excitations in molecular fluids is a problem of continuous interest. Developments in neutron, x-ray scattering and light scattering have revealed new aspects. Recently the existence of fast sound has been demonstrated in binary mixtures [1] and water [2]. Few studies, however, have documented the effect of high densities on the acoustic-like modes.

For gases under pressure, sound velocity can be measured by ultrasonic techniques on large samples in piston–cylinder devices, and by Brillouin light scattering [3], either on conventional optical cells below about 1 GPa, or in diamond anvil cells (DACs) up to very high-pressure. The first technique probes acoustic excitations with frequencies typically of 1–50 MHz, while the second one is sensitive to hyper-acoustic frequencies of the order of 1–10 GHz. This latter method, however, is the only possible one for very high-pressure samples such as those contained in a DAC. For hydrogen, high-pressure Brillouin light scattering measurements have been reported in the fluid [4], in the polycrystalline solid to 20 GPa [5], and, more recently, in a single crystal up to 24 GPa [6].

We present here new Brillouin results of fluid hydrogen at pressures from 50 MPa to 5 GPa, performed with a large-volume optical cell and with a diamond anvil cell. The goal of this new series of measurements is to assess the problem of dispersion in the sound velocity of fluid hydrogen at high pressure. Besides a fundamental interest, this problem has a very large practical importance for the derivation of the high-pressure equation of state of fluid from Brillouin measurements. In fact, the presence of sound dispersion may prevent the determination of the low-frequency, adiabatic sound velocity, which is the required quantity to derive, by means of integration, the pressure–density relation along an isotherm. Even for simple fluids this problem is not completely settled. In fact, evidence of a large negative dispersion measured in fluid argon and nitrogen has been recently reported [7].

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Dispersion of sound waves in polyatomic fluids has been the subject of much investigation in the past [8], and is mainly understood in term of relaxation of energy into internal (vibrational or rotational) degrees of freedom. From the frequency dependence of the sound speed and of the absorption coefficient, the relaxation times of thermal energy may be derived. When relaxation is present, the velocity of sound grows, for constant density, with increasing frequency (positive dispersion). Increasing density, however, the relaxation time decreases (in general proportionally to the inverse of density), and higher frequencies are then necessary to observe dispersion. It is expected, and observed in many polyatomic fluids, that the positive dispersion characteristic of relaxation phenomena disappears, increasing the density.

Relaxation is not the only cause of sound dispersion in a fluid. Solving the linearized hydrodynamics equation for a monatomic fluid, where no internal degrees of freedom exist, one reaches the following dispersion equation for the (complex) frequency s and (complex) wavevector k [9] of an acoustic excitation

$$s^3 + (a + b)k^2s^2 + (u_0^2k^2 + abk^4)s + au_0^2k^4/\gamma = 0 \quad (1)$$

where we have defined $a = \lambda/\rho c_v$ and $b = (\frac{4}{3}\eta_s + \eta_v)$, λ being the thermal conductivity, η_s and η_v the shear and bulk viscosity, ρ the density, c_p and c_v the heat capacity at constant pressure and at constant volume, u_0 the low-frequency sound velocity and $\gamma = c_p/c_v$. Equation (1) is solved as a series expansion of powers of the dimensionless quantities ak/u_0 and bk/u_0 , which, even for high values of k , like those in a light scattering experiment, are of the order of 10^{-2} . We recall at this point the discussion on the difference between an ultrasonic measurement and a light scattering experiment [9]. The two techniques are physically different. With light scattering one probes thermally excited plane waves (phonons), which have a wavevector fixed by the experimental conditions, and which are damped in time, but not in space. This corresponds to solving the dispersion equation for a complex frequency s as a function of a real k . The situation is reversed in an ultrasonic experiment. In that case one deals with driven sound waves, having a frequency fixed by the experimental conditions, and damped in space. The dispersion equation should then be solved for a complex wavevector k .

To first order the solution for the ultrasonic u_U and hypersonic (light scattering) u_H velocities are respectively [9, 10]

$$u_U = u_0 \left\{ 1 + \frac{1}{4} \left(\frac{\omega b}{u_0^2} \right)^2 \left[3 + 10(\gamma - 1) \frac{a}{\gamma b} - (\gamma - 1)(7 - 3\gamma) \left(\frac{a}{\gamma b} \right)^2 \right] \right\} \quad (2)$$

$$u_H = u_0 \left[1 + \frac{3\Gamma^2 + ab - 2\Gamma(a + b)}{2u_0^2} k^2 \right] \quad (3)$$

where we have used the definition of the sound absorption coefficient $\Gamma = \frac{1}{2}[b + a(1 - 1/\gamma)]$.

Equation (2) gives an increase of u_U with frequency, since, in general, the viscosity term b is larger than the heat conductivity term a (for hydrogen between 1 and 1000 bar $a/\gamma b \approx 4 - 5 \times 10^{-2}$) while the Brillouin hypersonic velocity u_H shows a negative dispersion, for physical values of the parameters. To our knowledge, this is the only theoretical prediction of a negative dispersion of sound excitations in a fluid. The value of this dispersion is however very small, for all simple dense fluids. For example, for hydrogen around 100 MPa, where γ , η_s and λ are known [11], and assuming $\eta_v = 270 \mu\text{Pa s}$ [19], one obtains a dispersion for hypersonic waves ($k \approx 1.8 \times 10^{-2} \text{ nm}^{-1}$) of about 3×10^{-4} , whose absolute value further decreases with the density.

In the case of fluid argon at room temperature, a recent Brillouin experiment [7] reports a negative dispersion of about 6% in the pressure range 200–600 MPa, in contrast with

previous Brillouin measurements, which reported a sound speed either in agreement [12] with ultrasonic measurements [13] or constantly higher [14] than the ultrasonic value.

Then, even for a system like argon, which is the prototype for a classical simple fluid, the situation is unclear. Dispersion of sound in simple fluids remains therefore an open problem, that only new experiments can clarify. Hydrogen and helium are certainly the two reference systems on which to perform these studies because of the simplicity of their interaction and also because at a given temperature the largest density domain in reduced units can be covered. Furthermore, the sound velocity in dense hydrogen provides direct constraints on the seismic structure of the molecular region of Jupiter. Very recently, a disagreement between Jovian global oscillation data and extrapolated or calculated sound velocity data was discussed [15].

For fluid hydrogen at room temperature, ultrasonic techniques (30 MHz) have been applied up to 2.0 GPa [16], extending the pressure range of previous measurements [17]. Brillouin light scattering measurements have been reported below 60 MPa [18, 19], and, more recently, extended in the range 0.6–5.5 GPa in a DAC [5], but the accuracy of the DAC data was questioned because of possible reactivity of hydrogen with the gasket material [6, 20]. Preliminary reports of Brillouin measurements by some of the present authors, in the fluid region at room temperature, have also appeared [21, 22]. A careful analysis of those data, performed recently, has demonstrated, in that case, an error on the pressure determination (due mainly to overheating of the ruby chip by the laser radiation). We will therefore disregard these data.

In contrast with other Brillouin experiments, where generally a Fabry–Pérot interferometer is used, here we have used a 2 m double-pass double monochromator [23] (SOPRA DMDP 2000) which attains a maximum resolution of 0.03 cm^{-1} . The excitation light was a single-mode argon ion laser beam, at a wavelength of 4880 \AA . This wavelength has been chosen because the Brillouin shift, being proportional to the excitation frequency, turns out in this case to be larger than when the 5145 \AA line is used, thus allowing a better detection of the signal. Always, both the Stokes and the anti-Stokes portions of the Brillouin spectrum have been recorded, scanning the monochromator in the same direction. The wavenumber shift of the Brillouin peak can be determined with a typical accuracy of 0.02 cm^{-1} . For the high-pressure runs (0.6–5 GPa), hydrogen is contained in a membrane DAC [24], at room temperature, within a rhenium or Be–Cu gasket. The incident beam enters the diamond at a 65° angle with respect to the normal. Due to the reflection of the laser light onto the internal surface of the diamond, light scattered at two different angles, i.e. in a quasi-forward and in a quasi-backward direction, has been collected. Therefore, two Brillouin peaks are observed both in the Stokes and in the anti-Stokes part of the spectrum. From the frequency positions of the two peaks, the value of both the refractive index and the hypersonic velocity can be obtained, provided the incidence and scattering angles in the laboratory system are known. These have been carefully measured, with a very small error (about 0.5°) whose influence on the final uncertainty on the speed of sound has been included in the error bar.

The refractive index n of hydrogen is known in the literature as a function of density ρ from measurements at low temperature [25]. These data are represented giving the density dependence of the Lorentz–Lorenz function r_λ as a polynomial in the density, plus a correction (the Cauchy formula) to take into account the wavelength dependence of the refractive index [26], namely

$$r_\lambda = \frac{1}{\rho} \frac{n^2 - 1}{n^2 + 2} = a + b\rho + c\rho^2 + d\rho^3 + \frac{A}{\lambda^2} + \frac{B}{\lambda^4} \quad (4)$$

where the parameters take the values $a = 0.0020245$, $b = 3.7171832 \times 10^{-7}$, $c =$

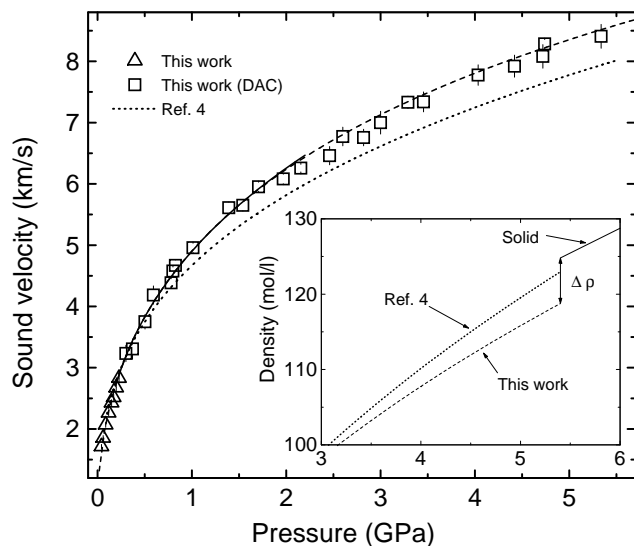


Figure 1. Sound velocity in hydrogen. The solid line represents the ultrasonic results [16], the open symbols are the present results (squares, in the DAC, triangles, in 90° geometry), which are fitted by the dashed line above 2 GPa. The dotted line represents the Brillouin result of [4] and [5]. In the inset we report the density derived from our sound velocity results (dashes), compared with the results of [4] and [5] (dots), and with the density of the solid [30] (full line).

$-9.208\,501\,3 \times 10^{-9}$, $d = -3.406\,532\,8 \times 10^{-12}$, $A = 1572.346\,326$, $B = 9.981\,443\,164 \times 10^8$ having expressed ρ in mol l^{-1} and λ in \AA . This formula is found to represent correctly also our measurements of the index of refraction at room temperature. This check has been made by calculating the density from the pressure by the use of the Mills equation of state of fluid hydrogen [16]. We have therefore used equation (4) to calculate the refractive index of hydrogen, with negligible uncertainty.

The pressure in the cell was measured by means of the shift of the fluorescence doublet of a small ruby chip, inserted in the sample. The fluorescence spectrum was recorded by a dedicated fixed-grating spectrometer, equipped with a cooled array detector. The instrument is calibrated each time with a neon spectral lamp. With this instrument, the peak position of the R_1 ruby line can be determined with a precision of 0.1 \AA , corresponding to a statistical uncertainty of 0.03 GPa . Particular care has been taken to avoid any heating of the ruby chip, keeping the laser power the lowest possible: much lower, in any case, than the threshold above which an increase may be detected in the wavelength position of the fluorescence peak. In the explored pressure range, the ruby pressure scale, that was calibrated against the NaCl equation of state [27], gives a precision of about 0.5% . The precision of the absolute pressure calibration is therefore of the same order of the uncertainty in the NaCl equation of state [28], which is 1.1% below 5.0 GPa . Our absolute pressure determination may be affected, therefore, by a systematic error, which however cannot be greater than 1.7% in this pressure range.

For the measurements in the pressure range $60\text{--}300 \text{ MPa}$, we have used a stainless steel high-pressure cell, equipped with three fused silica windows. The scattered light is collected at 90° , and the same spectroscopy apparatus as in the DAC case is used. The pressure, in this case, is measured with a calibrated pressure transducer. For both experiments the accuracy of the frequency shift measurements is 0.02 cm^{-1} .

In figure 1 we have plotted our Brillouin measurements of sound velocity in room-temperature fluid hydrogen, obtained either in the conventional cell or in the DAC (open symbols), compared with the ultrasonic data [16, 29] (solid line). In the same figure we report also the data obtained by Brody *et al* [4] (dotted line). We notice that, in contrast to what appears from the data of [4], no difference is observed between ultrasonic and Brillouin determinations of sound velocity, that is, no dispersion of sound waves is evident.

From the present sound velocity result, the density of the fluid can be calculated, with the relation $\rho(p) = \rho(p_0) + \int_{p_0}^p [\gamma / (U(p))^2] dp$. We have taken $p_0 = 2$ GPa, $\rho(p_0) = 86.256 \text{ mol l}^{-1}$ [16] and γ has been extrapolated, from the data of [16], as a slowly decreasing linear function of p . The resulting density can be represented by $\rho(p) = 68.978p^{0.321897}$, with p expressed in GPa and ρ in mol l^{-1} . From the density of the solid at melting [30] (assumed at 5.4 GPa) the difference of volume at melting turns out to be $\Delta V_m = 0.40 \pm 0.05 \text{ cm}^3 \text{ mol}^{-1}$, slightly above the functional form proposed in [31], on the basis of data up to 2 GPa. The density is reported in the inset of figure 1.

At lower density, Brillouin light scattering measurements have been reported by Hara *et al* [18] and by May *et al* [19]. To compare Brillouin and ultrasonic determination of the sound velocity in a large density range, in figure 2 we have plotted all the results on a logarithmic pressure scale. To display the differences between the Brillouin and the ultrasonic determinations of the sound velocity in all the pressure range, and to compare these with the error bars, we have reported in the inset the ratio between the Brillouin and the ultrasonic data.

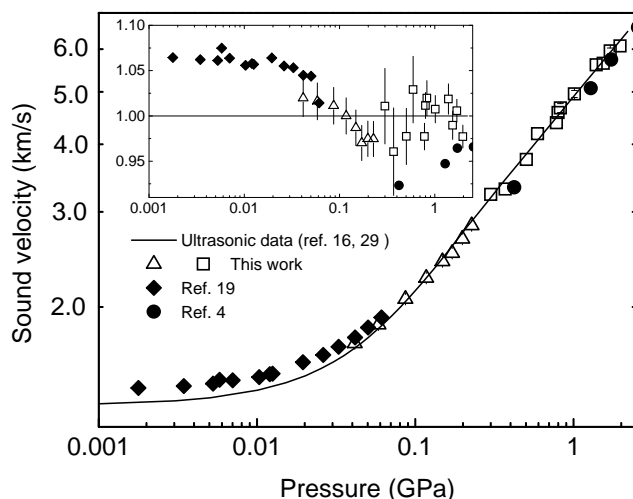


Figure 2. Sound velocity in hydrogen. Symbols are the Brillouin determination, while the solid line are ultrasonic measurements. In the inset we report the ratio of the Brillouin to the ultrasonic data.

The data of May [18, 19] (solid diamonds) show a positive dispersion at low density. This is interpreted in the framework of relaxation into internal (rotational) degrees of freedom, and is quantitatively reproduced by the theory of Mountain [32] and of Desai and Kapral [33]. Our data show that this dispersion decreases increasing pressure and disappears at about 100 MPa, indicating a faster relaxation as density increases.

The measurements in the DAC, even if with less accuracy, demonstrate that dispersion remain absent in the whole pressure range where comparison with ultrasound is possible,

that is, up to 2 GPa, and that high-density fluid hydrogen behaves in accordance with the standard hydrodynamic theory. From the sound velocity determination, it has been possible, therefore, to calculate the density of the fluid at room temperature, and the volume change at melting.

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