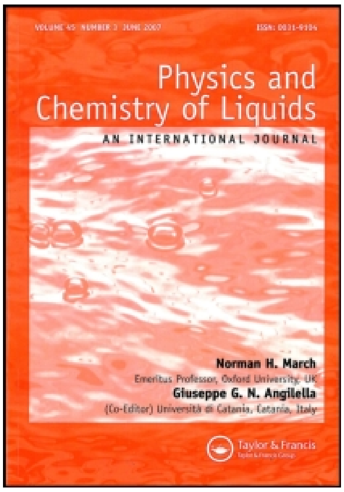

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L. Carraresi[a]; M. Celli[a]; F. Barocchi[a]
[a] Dipartimento di Fisica, Università di Firenze, Firenze, Italy

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THE RAYLEIGH-BRILLOUIN LIGHT SCATTERING SPECTRUM OF DENSE ARGON GAS BETWEEN 70 AND 260 MPa AT T = 298 K: THE SOUND VELOCITY AND THE SPECIFIC HEATS RATIO γ

L. CARRARESI, M. CELLI and F. BAROCCHI

Dipartimento di Fisica, Università di Firenze, Largo E. Fermi 2, Firenze, Italy

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Measurements of the Rayleigh–Brillouin spectrum in dense argon gas at $T = 298$ K and pressures between 70 and 260 MPa are reported. No dispersion in the sound velocity was found up to frequencies of the order of 4 GHz, and low and high frequency measurements agree within 0.5%. This permits the use of hypersonic velocity for deriving thermodynamic quantities for this system. From our measurements we have derived the density behavior of the specific heats ratio γ. Moreover, in absence of dispersion, we have shown that Brillouin scattering gives the sole possibility of measuring both the very low and high sound velocities in fluids, at the same time, therefore giving the direct possibility of checking either the absence or presence of dispersion.

KEY WORDS: Brillouin spectroscopy, thermodynamic properties

1 INTRODUCTION

Recently sound velocity measurements have been performed with conventional low frequency sound propagation methods in order to derive the equation of state of the gas and other thermodynamic properties. In noble gases, the maximum pressure has been reached in argon at about 1000 MPa[1]; in this case the precision of the measurements is quite high, of the order of 0.02%.

An alternative experimental method to ultrasonic propagation, for the study of the properties of collective excitations in fluids, is the Rayleigh–Brillouin scattering of light which is useful whenever the sample must be small in size, even though the precision, in this case, with respect to the ultrasonic propagation method is much lower.

Measurements of the Rayleigh–Brillouin spectrum in high pressure gases are of considerable interest because they allow to study the propagation of hydrodynamic collective excitation in the fluid at hypersonic frequencies, approximately two orders of magnitude higher than ultrasonic frequencies, and permit to study, if present, dispersion properties from the MHz to the GHz frequency range. These measurements can also give information about thermodynamic properties since some of these are connected with various spectroscopic features. For example, in the hydrodynamic regime in absence of dispersion, the hypersonic frequency is related to the compressibility, specific heats ratio and index of refraction and also the total Brillouin intensity is related to the same quantities. Moreover, one can notice that for simple fluids in a frequency-range in which the dispersion is absent the Brillouin spectrum, in principle, can give information, by means of independent measurements (frequency shift and integrated intensity of Brillouin peak), on both the hypersonic and low-frequency propagation velocity, which must be equal to each other. The possibility of measuring both velocities could be of interest in very high pressure systems. In fact in these systems is is very difficult to obtain the values of the adiabatic velocity by means of alternative experiments and so Rayleigh–Brillouin measurement is the only technique that permits to verify the absence of dispersion from the equality of hypersonic and low-frequency velocities. On the other hand, if dispersion is present in the fluid, the Rayleigh–Brillouin spectrum will show this presence since the relations of the spectral features with the thermodynamic quantities are not the ones valid in the hydrodynamic limit[3]. The advantage of the light scattering method is to permit the study of very small volume samples, reducing considerably also the size of the high-pressure apparatus allowing to reach very high pressures. Recently, hypersonic frequency measurements with Brillouin spectroscopy have been performed in Diamond Anvil Cells (DAC)[2] in the GPa region of pressures.

The experimental difficulty in the case of Brillouin spectroscopy of small samples is caused by the spurious elastically scattered light (stray light), due to the small size of the scattering cell, which obscures the spectrum and must be removed. Usually this is done with the help of either multipass or tandem Fabry–Perot interferometer.

Recently a new double monochromator[4] became available, namely the Sopra DMDP2000, which presents a high frequency resolution of ~0.75 GHz combined with a high degree of stray light rejection characteristic of these instruments. This monochromator is comparable with a tandem Fabry–Perot interferometer, even though the resolution is lower than usual Fabry–Perot, and can be used for Brillouin spectroscopy and studies of collective excitations with frequencies larger than ~1 GHz.

The DMDP2000 monochromator has two main advantages with respect to the multipass and tandem Fabry–Perot interferometer, (1) it is much easier to use, (2) it has a free-spectral range which is approximately 150 times bigger than the one of the previously named Fabry–Perot interferometers with the same resolution; in particular this last property is very important if one wishes to record Brillouin and Raman spectra of a sample with the same apparatus in order to compare their intensities for calibration purposes[5].

Here we will report the result of measurements of the Brillouin spectrum of argon gas at room temperature $T = 298$ K for pressures between 70 MPa and 260 MPa performed with the DMDP2000 monochromator, from which the density behavior of the frequency of hypersonic waves and of the integrated intensity of the Brillouin line can be determined with a good precision, of the order of 1–2% and 10% respectively.

The frequency of hypersonic waves is related to the index of refraction of the medium and to the velocity of the hypersonic waves v_h and throughout this last quantity, if no frequency dispersion is present in the propagation of collective excitations, i.e. when the hydrodynamic limit is valid, to the equation of state and all the related thermodynamic properties like the compressibility and the specific heats of the medium itself. In the case in which the equation of the state of the gas is known, the hypersonic frequency measurements can be used to determine the index of refraction.

Moreover, information on the ratio of the specific heats $\gamma = C_p/C_v$ can be derived from the intensities of the Rayleigh and Brillouin peaks. All these connections can therefore be studied in principle and hypersonic frequencies measurements used in order to determine some of those properties or to investigate their internal consistency.

2 THE RAYLEIGH–BRILLOUIN SPECTRUM AND THE THERMODYNAMIC PROPERTIES OF A FLUID

The spectrum $I(\omega)$ of quasi-elastic scattered light from a fluid medium, when no relaxation phenomena are present and the collective excitation of the system can be regarded as purely hydrodynamic, is given by the well known Rayleigh–Brillouin triplet[6]:

$$I(\omega) = \frac{C(n)K_B T\rho^2\beta_T}{\gamma}\left[(\gamma-1)\frac{D_T q^2}{\omega^2 + (D_T q^2)^2} + \frac{1}{2}\frac{\Gamma q^2}{(\omega - \omega(q))^2 + (\Gamma q^2)^2}\right.$$
$$+ \frac{1}{2}\frac{\Gamma q^2}{(\omega + \omega(q))^2 + (\Gamma q^2)^2}$$
$$\left. + \frac{1}{2}(\Gamma + (\gamma - 1)D_T)\frac{q}{v_h}\left(\frac{\omega + \omega(q)}{(\omega + \omega(q))^2 + (\Gamma q^2)^2} - \frac{\omega - \omega(q)}{(\omega - \omega(q))^2 + (\Gamma q^2)^2}\right)\right] \tag{1}$$

where

$$\beta_T = \frac{1}{\rho}\frac{\partial\rho}{\partial P}\bigg|_T \text{ is the isothermal compressibility}$$

$$\Gamma = \frac{1}{2}[(\gamma - 1)D_T + D_v] \text{ is the sound damping factor}$$

$$\gamma = \frac{C_p}{C_v} = \frac{\beta_T}{\beta_S}$$

$$\omega(q) = v_h q$$

$$\beta_S = \frac{1}{\rho}\frac{\partial\rho}{\partial P}\bigg|_S \text{ is the adiabatic compressibility}$$

C_p and C_v are the heat capacities at constant pressure and volume, respectively, D_T is the thermal diffusivity, D_v is the longitudinal kinematic viscosity, v_h is the hypersonic sound velocity, ρ is the numerical density, K_B is the Boltzmann constant and T is the temperature. The quantity $C(n)$ contains all the various constants which appear in the light scattering polarized intensity and depends on the density throughout the index of refraction n by means of two factors: one is due to the local field and can be approximated with the factor $((n^2 + 2)/3)^4$, the other is due to the scattered light collecting solid angle and goes as $1/n^2$ [7].

Therefore these thermodynamic and transport properties can be derived from experimental lineshape widths and peak frequencies measurements of the Rayleigh–Brillouin spectrum.

If the integrated intensity of the Rayleigh and the Brillouin lines are denoted by I_R and I_B respectively, then the following relation holds (Landau–Placzek ratio):

$$\frac{I_R}{2I_B} = \gamma - 1, \tag{2}$$

while the integrated intensities of the Rayleigh and the Brillouin peaks are given by:

$$I_R = C(n)K_B T\rho^2\beta_T\left(1 - \frac{1}{\gamma}\right) \tag{3}$$

$$I_B = \frac{1}{2}\, C(n)K_B T\rho^2\beta_T\, \frac{1}{\gamma} \tag{4}$$

There is a connection also between the low frequency velocity of sound and the various thermodynamic quantities which is given be the following well known relations:

$$v_s = \left(\frac{1}{m\rho\beta_S}\right)^{1/2} = \left(\frac{\gamma}{m\rho\beta_T}\right)^{1/2} \tag{5}$$

where m is the mass of a particle.

Therefore we can also write:

$$I_B = \frac{1}{2}\,\frac{C(n)K_B T\rho}{m v_s^2} \tag{6}$$

Here it is worth noticing that, in the absence of dispersion, Brillouin spectra measurements can give information, in principle, on both the low frequency sound velocity v_s and on the hypersonic sound velocity v_h, one from intensity measurements, Eq. (6) and the other from hypersonic frequency measurements. In the first case the knowledge of the density and $C(n)$ factors is needed, while in the second the knowledge of the index of refraction is required. However, measurements of v_s from I_B, are affected by large inaccuracy even though in some cases this could be the only available experimental possibility to measure v_s (in very high pressure systems, DAC). In principle the coefficient $C(n)$ can be measured if the intensity of an absolutely calibrated spectroscopic line can be measured with the same apparatus which is used for the Rayleigh–Brillouin spectrum; therefore in this case also absolute values for the sound velocity can be given. This calibration could be done in much the same way that is done for DILS spectroscopy[7]. If absolute calibration is not made then, from the knowledge of the density behavior of n and, consequently, of $C(n)$, only the density behavior of v_s can be given.

From measurements of the hypersonic frequency shift $\omega(q)$ and knowing the density behavior of the refraction index of the gas, one can derive the hypersonic sound velocity and verify either the presence or absence of dispersion in comparison to the low frequency sound velocity. Moreover, in the absence of dispersion, by means of the hypersonic sound velocity, one can derive the specific heats ratio γ, Eq. (5). As previously mentioned, γ can also be derived from measurements of the intensities of the Rayleigh and Brillouin peaks, Eq. (2), however this is more difficult because of stray light contribution to I_R.

In the following we will show the hypersonic frequency and spectral intensities measurements, performed with this new monochromator, we will give the results for the argon gas at room temperature and pressures between 70 and 260 MPa and show some possibility of use of the measurement in order to derive informations on other quantities.

3 EXPERIMENTAL APPARATUS AND MEASUREMENTS IN ARGON UP TO 260 MPa

The apparatus we used in our experiment was a typical one for Raman spectroscopy. It consists or an argon ion laser operating on a single mode configuration at the wavelength 4880 Å, the focusing and collecting optics and the DMDP2000 monochromator equipped with single photon counting detection apparatus. The noise of the detection apparatus was ~ 0.5 cps.

The DMDP2000 can be used in different configurations from single pass to quadruple pass. Increasing the number of passes increases the resolution but diminishes both the intensity which reaches the detector and the stability of the apparatus. A good compromise in our case was to work in triple pass configuration with an instrument resolution of 1.8 GHz.

The high pressure optical cell was built in our laboratory and consists of a small body of $3.5 \times 5 \times 2$ cm with three high pressure fused quartz windows. The windows were cylinders of diameters 4.7 mm and high 5 mm, the sealing of the windows was made with epoxy glue (STYCAST 2850 FT and Catalyst 24 LV, GRACE Electronic Materials) while the windows holder was sealed to the body with metal to metal contact.

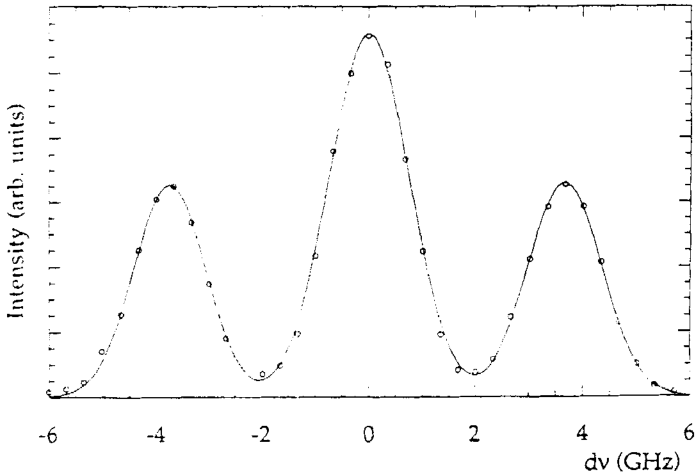

Figure 1 Typical experimental spectrum of argon at $T = 298$ K, $\rho = 18.9$ atoms/nm^3. The line represents the instrumental line fit of the experimental spectrum.

The spectra were recorded in a geometry at 90 degree between the incoming and scattered light.

The Rayleigh–Brillouin spectrum of argon was measured at $T = 298 \pm 1$ K at 25 different pressures, from 70 to 260 MPa, which correspond to densities from 12.64 to 19.63 atoms/nm^3. Pressures were measured with a transducer with a precision of $\sim 0.2\%$. For the determination of the densities we used the equation of state of Michels *et al.*[8]. A typical experimental spectrum is given in Figure 1.

All the measured spectra were fitted to the monochromator resolution function and the peak frequencies and integrated intensities of the various peaks were derived from this fitting. The frequency range of the hypersonic waves detected in the experiment was between 2 and 4 GHz for pressures between 70 and 260 MPa.

Using the relation between the frequency $\omega(q)$ and the velocity of sound and the values of the index of refraction of argon at our thermodynamic states[9], we have derived the behavior of the hypersonic sound velocity as a function of density for argon at $T = 298$ K. Figure 2 gives the behavior of the measured hypersonic sound velocity together with some values of the ultrasonic sound velocity given in literature[1].

Since a small amount of density dependent stray light ($\sim 20\%$) contributes to the intensity of the central peak in our experiment, the ratio $I_R/2I_B$ could not be determined. Nevertheless the intensity I_B could be measured and it is given, in arbitrary units, in Figure 3. From our measurements we noticed that the hypersonic sound velocity can be given with an error of ~ 1–2% while the integrated intensity of one of the Brillouin line is given with an error of $\sim 10\%$.

4 DISCUSSION

In order to compare our hypersonic sound velocities with the ultrasonic sound velocities of Ref. 1, which are performed at different densities, we have least square

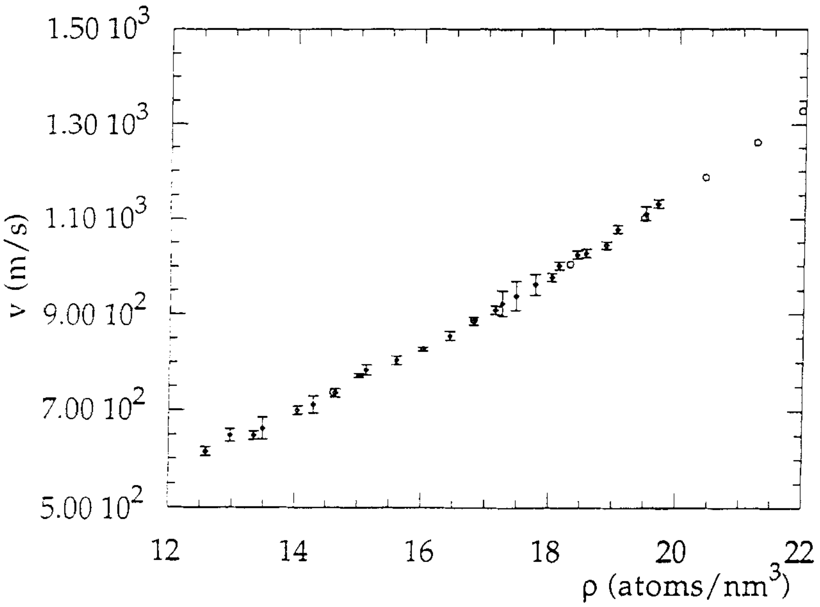

Figure 2 Density behavior of the hypersonic sound velocity from this experiment, open diamonds, and of ultrasonic sound velocity from Ref. 1, open circles.

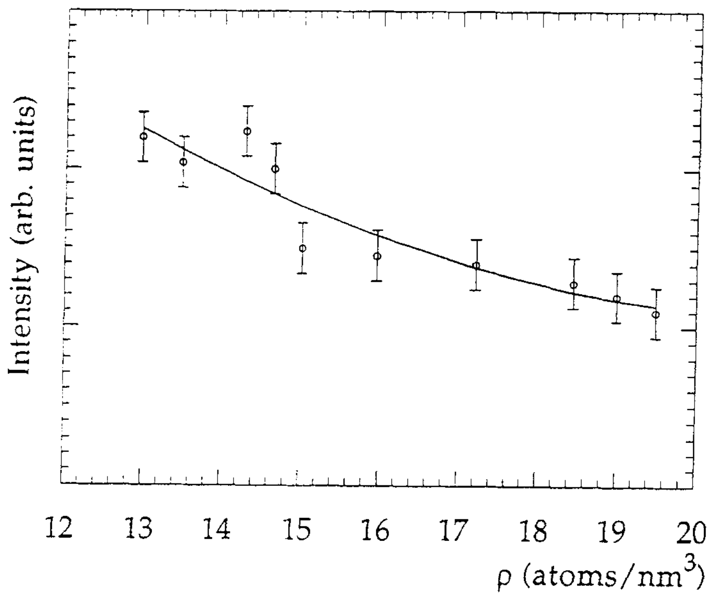

Figure 3 Density behavior of the integrated intensity of the Brillouin peak, in arbitrary units. The line represents the fit of the experimental data with a quadratic power law.

fitted our data with various density polynomials. The fit with the best χ^2 was found for a quadratic equation.

This function gives hypersonic values which are within 0.5% from the ultrasonic values given in Ref. 1. This means that in argon gas at the experimental densities any possible velocity dispersion, in the frequency range explored, i.e up to 4 GHz, is less than 0.5%.

By means of the density dependence of the hypersonic sound velocity obtained from a quadratic least square fit to our experimental data, and of the equation of state[8] we can now derive the specific heats ratio $\gamma = \beta_T/\beta_s$ at various density points. This is given for argon in Figure 4 at our experimental densities where our values are compared with published values, one of which is derived from the equation of state[10], and the others from ultrasonic sound velocity[11]. Our values and the values of Refs. 10 and 11 differ less than 1%.

As we have pointed out before by means of the experimental values of the integrated intensity of one of the Brillouin lines it is possible to derive information also on the low frequency sound velocity, in particular in our case since absolute intensity calibration has not been performed, we can derive only the density behavior of v_s. This is done by means of Eq. (6), knowing the density behavior of $C(n)$ from its n dependence and by using the index of refraction of argon given in Ref .9.

Figure 5 gives the density behavior of v_s, in the measured density range, derived from the density dependence of a quadratic least square fit to the experimental $I_B(\rho)$.

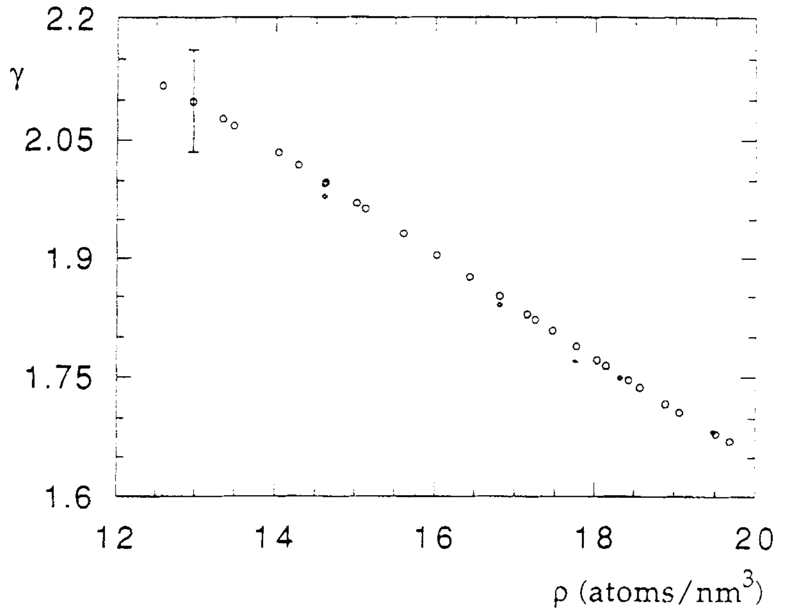

Figure 4 Density behavior of the specific heats ratio γ from our experimental data of hypersonic sound velocity, open circles. The open square is a value of γ from Ref. 10 and the open diamonds are data from Ref. 11. The bar indicates a typical experimental error.

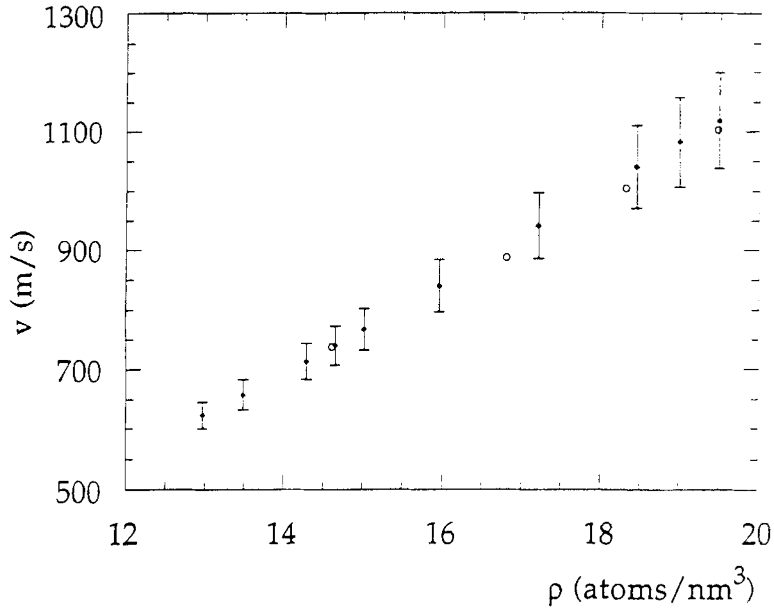

Figure 5 Density behavior of sound velocity, derived from the integrated intensity I_B, (see text), open diamonds compared with ultrasonic sound velocity[1], open circles. Notice that from I_B we have obtained only the density behavior of the sound velocity in arbitrary units. The comparison with the ultrasonic velocity is realized by equalizing the two velocities at $\rho = 14.7$ atoms/nm^3.

Our data are compared with the known values of v_s given in Ref. 1 and show that, even though with large uncertainty, the Brillouin line intensity can be used for giving a measure of the low frequency sound velocity.

In conclusion we have shown that the measurement of the Rayleigh–Brillouin spectrum in dense gases can be performed with a new double monochromator and give hypersonic sound velocities with good precision. In particular for argon gas at $T = 298$ K and pressures between 70 and 260 MPa, we have found no dispersion in the sound velocity up to frequencies of the order of 4 GHz and low and high frequency measurements agree within 0.5%. This permits, within the previous accuracy, the use of hypersonic sound velocity for deriving thermodynamic quantities of argon gas. From our measurements we have also derived the density behavior of the specific heats ratio γ. Moreover we have shown that from Brillouin intensity measurements the low frequency sound velocity can be derived giving to Brillouin spectroscopy the sole possibility of measuring both the very-low and high frequency velocities in fluids.

This method could be used for example in diamond anvil cells in order to detect either the absence or presence of sound dispersion.

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