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Sound Velocity and Sound Attenuation Measurements by Dynamic Light Scattering[1]

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Dynamic light scattering (photon correlation spectroscopy) has been applied to the determination of sound velocity and sound attenuation from the Brillouin component of the frequency spectrum scattered from a fluid sample transversed by a laser beam. In this paper the time-resolved determination of the Brillouin component is described. The measurement of the linewidth allows an accurate determination of the sound attenuation, while the central frequency is connected to the adiabatic sound velocity. Sound attenuation and sound velocity measurements are presented for the new refrigerant pentafluorethane (R125). The accuracy and possible systematic errors of this technique are discussed and compared to those obtained from other spectroscopic and acoustic techniques.

KEY WORDS: Brillouin spectroscopy; dynamic light scattering; R125; sound attenuation; sound velocity.

1. INTRODUCTION

From hydrodynamics and statistical thermodynamics it is well known that, in thermodynamic equilibrium, transport phenomena take place due to the random fluctuations of the thermodynamic variables on the molecular scale. These processes in average follow exactly the same laws as the macroscopic processes studied in traditional experiments [1].

Several thermophysical and thermodynamic properties can be determined from the spectrum of laser light scattered from the hydrodynamic modes of a fluid. Thus, from the Rayleigh line the thermal diffusivity and the mutual diffusion coefficient of binary mixtures are routinely determined

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with high accuracy over an extended range of temperature and pressure using dynamic light scattering [2]. During the past few years, the sound velocity and sound attenuation of the fluid have been obtained from the Brillouin component of the spectrum. Based on our experimental results for the refrigerant R125, we will discuss the way in which the measurements are affected by dispersion effects, which always have to be considered carefully when measuring sound velocity and sound attenuation. Furthermore, it will be shown that with this technique an accurate determination of the sound attenuation is possible without any corrections due to the finite aperture of the detection optics.

2. METHOD

If a fluid sample is irradiated by a laser beam, light is scattered in all directions from local fluctuations of the dielectric constant. For a pure simple fluid, the spectrum of this scattered light consists of three contributions: the central, unshifted Rayleigh line and two symmetrically shifted Brillouin lines [1], as shown in Fig. 1. The asymmetry of the Brillouin lines which shifts the maximum toward the center frequency is usually very small [1] and thus neglected here. The central line is caused by entropy (temperature) fluctuations, and its width is proportional to the thermal diffusivity D_T. The two adjacent Brillouin lines are caused by pressure fluctuations and are frequency shifted due to the Doppler effect, by

$$\Delta\omega_B = \pm c_s q, \qquad \nu_B = \frac{\Delta\omega_B}{2\pi} \tag{1}$$

with c_s the adiabatic sound velocity of frequency ν_B and q the modulus of the scattering vector defined as

$$q = \frac{4\pi n}{\lambda_0} \sin\frac{\Theta_s}{2} \tag{2}$$

Here n is the refractive index of the sample, λ_0 the laser wavelength in vacuum, and Θ_s the scattering angle.

The detection of the spectrum can be performed in two different ways. By means of a high-resolution Fabry–Perot spectrometer, the spectrum can be obtained by resolving the frequency. Because the linewidth decreases with decreasing scattering angle, such experiments are usually performed at a detection angle of 90°, which leads to measurement frequencies of several GHz. Here, in general, significant dispersion is observed for both sound

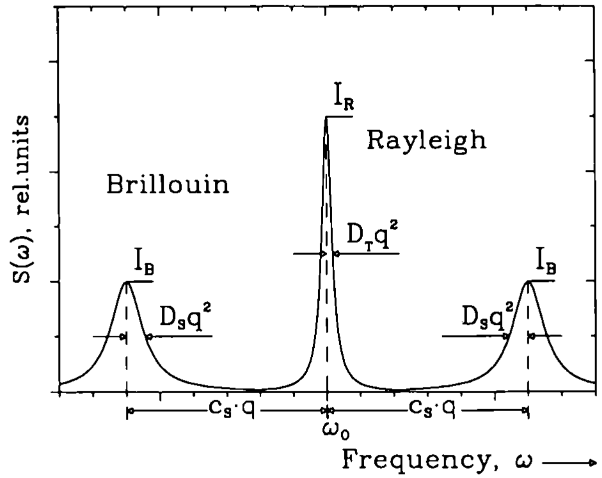

Fig. 1. Power spectral density of a pure fluid.

velocity and sound attenuation, resulting in sound velocities higher than the thermodynamic value [3]

$$c_s^2 = \left(\frac{\partial p}{\partial \rho}\right)_s \tag{3}$$

The width and central frequency of the Brillouin line can also be measured in a different way that permits access to smaller measurement angles and therefore to smaller frequencies in the MHz range. This method

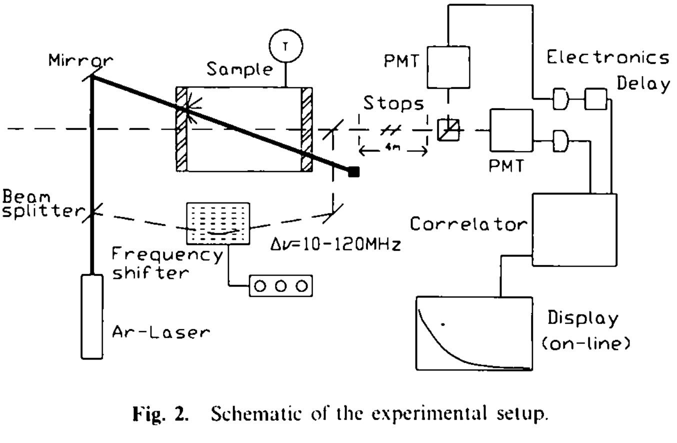

Fig. 2. Schematic of the experimental setup.

is the time-resolved detection of the scattered light by which the correlation function of the time-dependent signal intensity is computed. Here, the inverse Fourier transform of the spectrum is measured. For simple fluids this leads to an exponentially decaying function, with the decay time inversely proportional to the linewidth [1, 4].

A favorable way of detecting the Brillouin line by dynamic light scattering is the heterodyne technique, which uses a frequency-adapted background [5]. The experimental setup is shown schematically in Fig. 2. It is described in detail elsewhere [6].

A laser beam (argon-ion laser in single mode at 488 nm) is directed into the sample. The scattered light is detected by two photomultiplier tubes (PMTs) in photon-counting mode. The two signals are cross-correlated by a correlator (Malvern 7025 single-tau correlator). This leads to a suppression of dead-time effects and after-pulsing effects that would disturb the correlogram at short times, where the Brillouin signal is detected. The scattering angle can be measured accurately by means of autocollimation [7]. Part of the incident laser light is frequency-shifted by means of an acousto-optical modulator and superimposed on the sample signal as a local oscillator. If the frequency difference between the Brillouin shift and the frequency shift of the modulated reference light is not too large, the correlation function has the form of a damped oscillation

$$G(\tau) = A + B\exp(-\tau/\tau_c)\cos(2\pi\,\Delta\nu\,\tau) \tag{4}$$

The decay time of the oscillation is inversely proportional to the Brillouin linewidth

$$\tau_c = \frac{1}{\omega_B} = \frac{1}{D_s q^2} \tag{5}$$

Here, ω_B is the Brillouin linewidth, D_s is the sound attenuation constant, and $\Delta\nu$ is the difference of the Brillouin shift ν_B and the modulator shift frequency $\Delta\nu_M$,

$$\Delta\nu = \mathrm{abs}(\nu_B - \Delta\nu_M) \tag{6}$$

From the measurement the frequency of the oscillation can be evaluated with high accuracy when a suitable evaluation procedure is used [8]. Combining Eqs. (1) and (6), one can calculate the sound velocity.

The sound attenuation constant is related to the more commonly used quantity α_s/ν_s^2 by

$$D_s = 1/(2\pi)^2\,(\alpha_s/\nu_s^2)\,c_s^3 \tag{7}$$

where ν_s is the sound frequency and α_s is the absorption coefficient. The sound attenuation is dependent on the shear and bulk viscosities η_s and η_v.

3. RESULTS AND DISCUSSION

To the best of our knowledge, there is only one recent publication in which the sound velocity of saturated R125 can be found [9]. A comparison shows an agreement within ±0.5% for the sound velocity of the saturated liquid within the temperature range of the measurements [10]. The aim of this paper is to discuss the precision of the sound velocity measurements by dynamic light scattering and the estimation of systematic errors in the determination of the sound attenuation when applying different measurement techniques.

To test the influence of the measurement frequency on the sound velocity, the frequency of the detected sound waves can be varied with the detection angle and laser wavelength [6] according to Eqs. (1) and (3). A typical result of such an experiment on saturated pentafluorethane (R125) at 45°C is shown in Fig. 3. In addition to the measurement results, the solid lines indicate the ±0.5% error region, while the dashed lines indicate the error which would result from an angle inaccuracy of 0.02°. Obviously no dispersion effect can be recognized. Furthermore, the reproducibility of the single measurements for the different frequencies is better than 0.5%, indicating the quality of the angle measurement and of the evaluation procedure. Thus, a dispersion of the sound velocity of the order of 0.5% in the adjustable frequency range will be detectable by this technique. This will become important when the critical point is approached, because a decrease of the dispersion frequency is expected [11]. The precision of the determination of the central frequency can in principle be enhanced due to statistical reasons by taking a large number of independent single measurements. The precision of the sound velocity will then be limited by the possible deformation of the Brillouin lines due to intermolecular relaxation processes [1] and dispersion.

When measuring the linewidth of the Brillouin component, corrections have to be made to include the finite aperture of the detection optics [12]. Simple geometric considerations show that the optical path through the two stops which define the direction of observation gives rise to a lack of definition of the measurement angle. Neglecting diffraction, the maximum range of the detected angle area can be estimated by

$$\Delta\Theta = \Theta_s \pm \Delta\vartheta; \qquad \Delta\vartheta \approx \frac{1}{2}\frac{d_1 + d_2}{R} \tag{8}$$

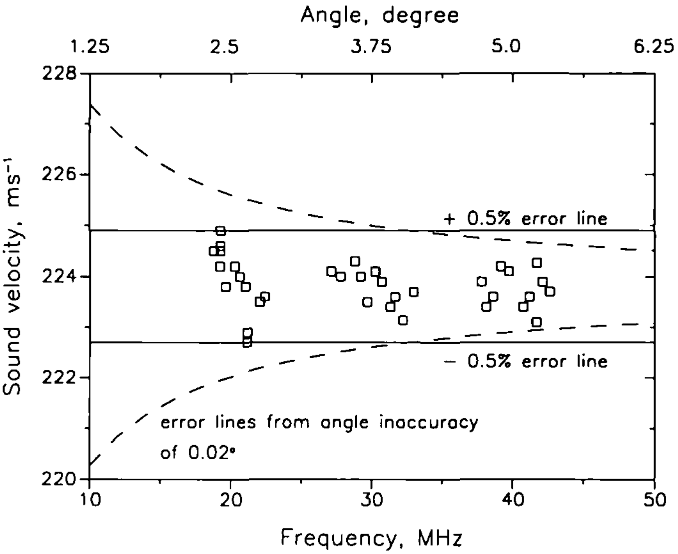

Fig. 3. Measured sound velocity of saturated R125 as a function of frequency.

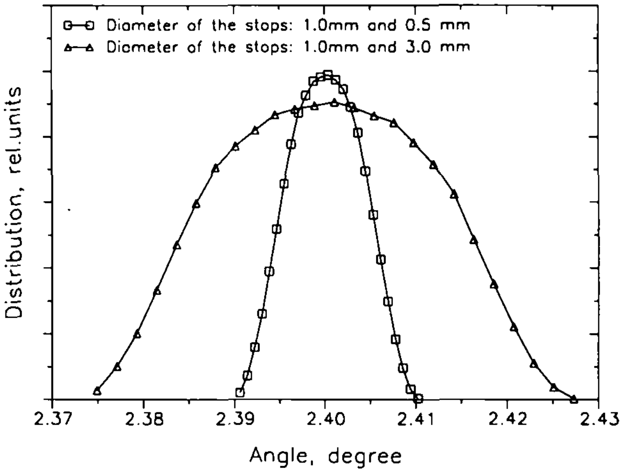

Fig. 4. Spread of geometrical angle due to the poor definition of measurement angle because of the finite diameter of the stops.

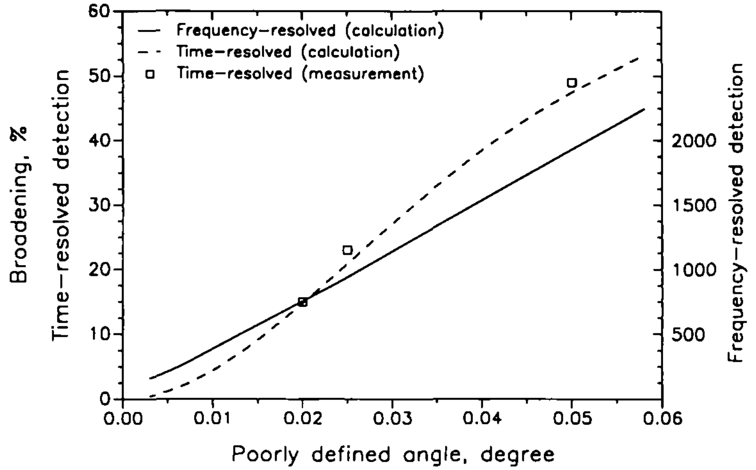

Fig. 5. Dependence of the measured decay time for sound attenuation measurements on the stop diameter used, compared with expected behavior for frequency-resolved and time-resolved measurement techniques. $\theta_c = 3°$; $c_s = 190\ \mathrm{m \cdot s^{-1}}$; $D_s = 1.5 \times 10^{-6}\ \mathrm{m^2 \cdot s^{-1}}$.

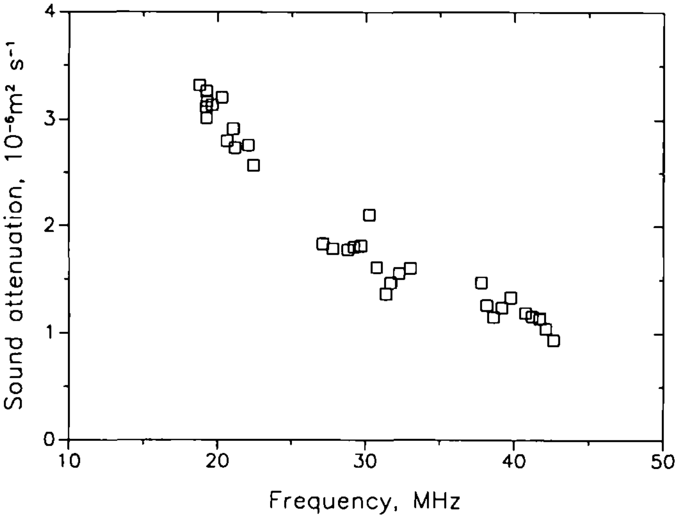

Fig. 6. Sound attenuation of saturated R125 at 45°C as a function of frequency.

Here, d_1 and d_2 are the stop diameters and R is the distance between the stops. As an example, the range of detected angles as a function of the stop diameters is shown in Fig. 4. The curves show the results of the calculation of the range of detection angles when equidistant points within the free diameter of one stop are connected geometrically with those of the second stop which is placed at a distance of 4 m away from the first stop.

If the diameter of the first stop behind the sample cell is small, the detected angle area is determined by diffraction and can be estimated by

$$\Delta\vartheta \approx \frac{\lambda_0}{d_1} \tag{9}$$

According to the detected angle area, all possible Brillouin lines due to these angles are detected simultaneously, resulting in one observable line. In the frequency domain, this leads to a significant line broadening because the shift of the central frequency as a function of this change of angle can be larger than the linewidth itself. In dynamic light scattering this line broadening effect is smaller because the superposition of damped oscillations with different frequencies has a smaller effect on the decay time than the superposition of shifted lines in the frequency domain. Figure 5 shows the measured and calculated change of the decay time of the Brillouin component of saturated R125 at 50°C for a detection angle of 3 deg as function of the poorly defined angle. The calculated trend of results for the linewidth from frequency-resolved measurements without correction is indicated in the same figure. The difference between the two techniques is larger than one order of magnitude.

For this example, the effect of line broadening is well below the measurement uncertainty of approximately 5–10% [13] when the poorly defined detection angle ($\Delta\vartheta/\Theta_s$) is of the order of 5×10^{-3}. In contrast to frequency-resolving techniques, and contrary to statements reported in the literature [5], dynamic light scattering seems to allow a precise determination of the low-frequency Brillouin spectrum almost free of systematic errors due to line broadening. Only in this way is it possible to perform measurements in the low-frequency region of optical spectroscopy, because the influence of superimposed diffraction and the geometrical lack of angle definition can hardly be calculated accurately enough to gain good results for sound attenuation with frequency-resolving methods.

As an example, Fig. 6 shows the data evaluated from the decay times of the sound velocity measurements shown in Fig. 3. Here, in contrast to the sound velocity, a significant frequency dispersion, well above the magnitude of line broadening, is obtained indicating a frequency-dependent bulk viscosity, which for nonsimple fluids such as refrigerants has been expected in the literature [1].

4. CONCLUSIONS

The results presented in this paper indicate that dynamic light scattering permits the determination of the low-frequency Brillouin spectrum with high precision. From such measurements the sound velocity can be extracted. For fluids without intermolecular coupling to density fluctuations, the bulk viscosity can be studied in this way. For fluids that have such coupling, the dynamics of intermolecular relaxation processes may be determined by measuring the frequency dependence of the sound attenuation.

Especially near the critical point, the change in sound attenuation and sound velocity as functions of reduced temperature and frequency promises to yield interesting results and a useful addition to available acoustic and other spectroscopic measurement techniques for the determination of the sound velocity and the sound attenuation. The results presented in this paper show that this method should be able to determine spectroscopically the position and the width of the Brillouin line at frequencies which were not accessible up to now.

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