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Brillouin scattering from liquid CCl_4 at high pressures

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Brillouin spectra were obtained from liquid carbon tetrachloride at pressures ranging from 1 to 1500 bar and at three temperatures (298, 323, and 348 K). Using Mountain's theory the relaxation time τ_v of the bulk viscosity and the energy relaxation time $\tau_E = C_v \tau_v / (c_v - c_l)$ were derived from the experimental spectra. At constant temperature τ_E decreases with increasing density, and at constant density τ_E decreases with increasing temperature. From τ_E the effective collision diameter was calculated for hard spheres (HS): $\sigma_{\text{HS}} = 5.24 \pm 0.05 \text{ \AA}$.

I. INTRODUCTION

In many so-called simple, polyatomic liquids such as CS_2 , CO_2 , CCl_4 , and CHCl_3 , the main contribution to ultrasonic absorption stems from vibrational relaxation. This damping mechanism of acoustical energy is due to a delayed exchange of energy between external (translational, rotational) degrees of freedom and internal vibrations of the molecules. The exchange of energy occurs through collisions between the molecules in the liquid. Therefore, the time τ_E necessary to reach thermal equilibrium in the liquid is a function of the number of collisions per unit time (N) and of the probability (P) of the excitation of vibrations. In comparison with gases the number of collisions per unit time in liquids is several orders of magnitude higher due to the fact that the mean free path is small. From this it follows that the relaxation times in the liquid state are shorter by a factor of the order of 10^3 . For example, the energy relaxation time τ_E in gaseous CCl_4 is $208 \mu\text{sec}^{-1}$ at 1 bar and 303 K and $160 \text{ psec}^{2,3}$ in liquid CCl_4 . Therefore the study of vibrational relaxation in liquids compared to gases by ultrasonic methods (time scale from 10^{-5} to 10^{-9} sec) is successful in only a few cases (CS_2).

By means of Brillouin scattering frequencies of 10^9 to 10^{10} Hz can be achieved as required for relaxation measurements in liquids. Although much work has been done on Brillouin scattering in liquids at atmospheric pressure, up to now there have been only a small number of papers³⁻⁵ on Brillouin scattering in liquids at high pressures.

The purpose of this study was to observe the density dependence of τ_E at constant temperature and to derive the temperature dependence of τ_E at constant density. Therefore the pressure dependence was measured at the three temperatures for which ultrasonic data of CCl_4 at high pressures could be found in literature.

II. EXPERIMENTAL DETAILS

The green line at 514.5 nm of an argon ion laser (Spectra Physics Model-165) with a power of 200 mW in single mode operation was used for the measurements. The

single mode operation was controlled by a spectrum analyzer. The liquid carbon tetrachloride (Uvasol by Merck) was contained in a three-window high pressure cell with a 90° scattering configuration described elsewhere.⁶ This cell was surrounded by a thermostat to achieve a temperature constancy of $\pm 0.2^\circ\text{C}$ in the liquid. The scattering angle was $90^\circ \pm 20'$.

The liquid itself was used as a pressure medium. Because of the aggressiveness of carbon tetrachloride a special fluid divider was designed. This fluid divider, (basically a 1:1 intensifier with easy-to-exchange Teflon packings which are not destroyed by the corrosive fluid) allowed the use of oil as pressure medium on one side and any liquid pressure medium on the other.

High pressure was generated using a hand pump up to 700 bar, and up to 2000 bar using a hand screw press. All high pressure tubing and parts filled with carbon tetrachloride were heated to prevent solidification of the CCl_4 at high pressures. Pressure was measured with a Bourdon manometer with an error of ± 10 bar and with a temperature-compensated manganin cell with an error of ± 12 bar. The scattered light was analyzed with an electronically stabilized⁷ five-pass Fabry-Perot interferometer, which makes it possible to detect the Mountain peak more exactly because of the high contrast of this instrument.

A multichannel analyzer allowed the multiple scanning necessary for an acceptable signal-to-noise ratio. The scattered light was detected with a cooled photomultiplier with a dark count rate of 3 counts/sec. The spectra were stored in the multichannel analyzer and printed on punched tape.

The relaxation time τ_v was determined from any experimental Brillouin spectrum by fitting theoretical Brillouin spectra⁸ to it, taking into account the influence of the instrumental function. A PDP-15 computer was used for these calculations. Values for the hypersound velocity v_H and the half width Γ_B of the Brillouin line were also taken from the best theoretical fit using Mountain's theory.⁸

In order to calculate the theoretical Brillouin spectra, we had to take or derive the following data from literature: density ρ ,¹⁰⁻¹² sound velocity v_0 at the limit of low frequencies,¹⁰⁻¹³ ultrasonic absorption α/f^2 at the limit of low frequencies,^{10,13} thermal conductivity λ ,¹⁴ refractive index¹¹ n , shear viscosity η_S ,^{9,15,16} and specific heat at constant pressure C_p . The nonrelaxing bulk viscosity¹⁷ $\eta_{B,\infty}$ was assumed to be equal to the shear viscosity.

III. RESULTS AND DISCUSSION

Figure 1 shows the Brillouin spectra of CCl₄ at 323 K and at pressures of 1 and 1500 bar, respectively. One can clearly recognize the increasing half width of the Mountain peak with increasing pressure, indicating that the relaxation time τ_V of the bulk viscosity gets shorter. As already pointed out, the theoretical one-parameter fit (Sec. II) to experimental Brillouin spectra as shown in Fig. 1 yields the relaxation time τ_V of the bulk viscosity.

The values of τ_V as function of pressure at constant temperatures are shown in Fig. 2. The error in the measurements is ± 2.5 psec.

For the three temperatures shown, τ_V decreases with increasing pressure. It is also apparent that the relaxation time decreases with increasing temperature. The energy relaxation time τ_E is connected to τ_V by the relationship

$$\tau_E = \tau_V C_v / (C_v - C_i) , \quad (1)$$

where C_i is the specific heat according to the Planck-Einstein formula

$$C_i = R \sum_j l_j x^2 \frac{e^x}{(e^x - 1)^2} \quad (2)$$

with $x = h\nu_j/k_B T$. Here R is the gas constant, l_j the degeneracy of the j th vibration, h the Planck constant, and ν_j the frequency of the j th vibration. C_v is the specific heat at constant volume.

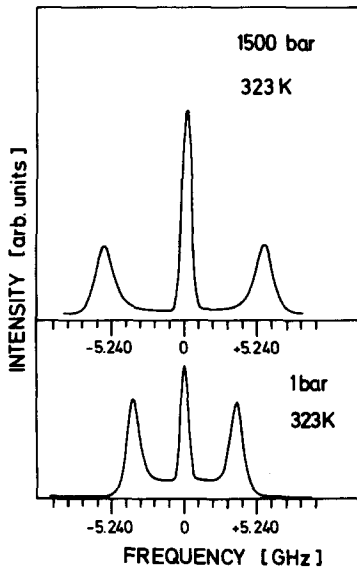


FIG. 1. Brillouin spectra at 323 K and at pressures of 1 bar and 1500 bar, respectively.

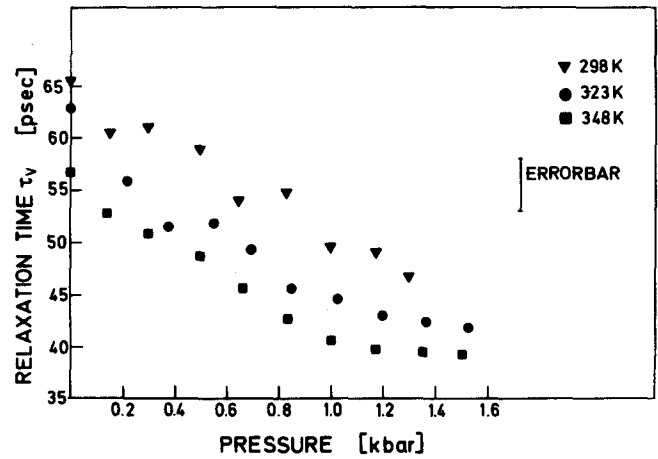


FIG. 2. Relaxation time τ_V of the bulk viscosity of liquid CCl₄ versus pressure at constant temperatures.

The CCl₄ molecule has four different vibrational degrees of freedom with the following frequencies: $\nu_1 = 458$ cm⁻¹, $\nu_2 = 218$ cm⁻¹, $\nu_3 = 776$ cm⁻¹, and $\nu_4 = 314$ cm⁻¹. ν_2 is doubly degenerated; ν_3 and ν_4 are triply degenerated.

C_v is necessary for calculation of τ_E from Eq. (9), but no experimental values of C_v at high pressures are available. Fortunately, C_v can be determined from C_p , C_i , and the dispersion v_∞^2/v_0^2 where v_∞ is the high frequency limit of sound velocity.¹⁸ v_∞ is related to the sound velocity v_H , which can be determined experimentally from the Brillouin spectra using

$$v_\infty^2 = (v_H^2 - v_0^2) [(1 + \omega_B^2 \tau_V^2) / \omega_B^2 \tau_V^2] + v_0^2 , \quad (3)$$

where ω_B denotes the Brillouin shift

$$\omega_B = v_H k , \quad (4)$$

where k is the absolute value of the wave vector given by scattering geometry. Furthermore, one has¹⁸

$$v_\infty^2/v_0^2 = 1 + (C_p - C_v) C_i / (C_v - C_i) C_p . \quad (5)$$

Using this relation, one can calculate C_v .

$(C_p - C_v) C_i / (C_v - C_i) C_p$ can also be determined from Eq. (6).

$$\eta_{B,rel} = \rho v_0^2 \tau_V [(C_p - C_v) C_i / (C_v - C_i) C_p] , \quad (6)$$

where $\eta_{B,rel}$ is the relaxing contribution of the bulk viscosity η_B . $\eta_{B,rel}$ can be calculated from the ultrasonic absorption using the relation¹⁸

$$\alpha/f^2 = (2\pi^2/\rho v_0^3) (\frac{4}{3} \eta_S + \eta_{B,\infty} + \eta_{B,rel}) . \quad (7)$$

The values of C_v calculated with Eqs. (5) and (6) agree within $\pm 1\%$.

Finally, Fig. 3 shows the energy relaxation time τ_E at constant temperature against the mean distance d of the molecular centers. d is given by

$$d = 2^{1/6} (M/\rho N)^{1/3} , \quad (8)$$

where M is the molecular weight, ρ the density, and N Loschmidt's number. The error in the energy relaxation times in Fig. 3 is ± 7 psec.

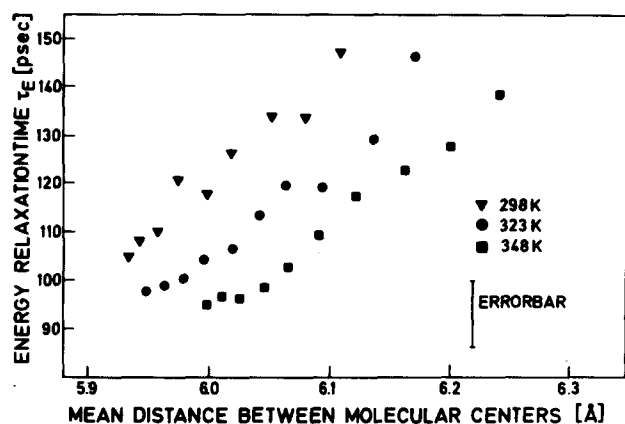


FIG. 3. Energy relaxation time τ_E of CCl₄ versus the mean distance between molecular centers at constant temperatures.

At constant temperature τ_E increases with increasing mean distance of the molecular centers. Because of the indirect density dependence of d , τ_E decreases with increasing density at constant temperature. At constant density (constant d) τ_E decreases with increasing temperature. The observed decrease of τ_E can be explained by an increasing transition probability P with increasing temperature at constant density.

In order to find an effective hard sphere diameter of liquid CCl₄ for the vibrational-translational energy exchange the relation $\tau_E = 1/(NP)$ was used. P was assumed to be independent of pressure¹⁹⁻²¹ and \bar{N} was calculated by an equation for the collision rate of hard spheres given by Einwohner and Alder.²² The data points of τ_E fitted to this equation yield a hard sphere diameter $\sigma_{HS} = 5.24 \pm 0.05$ Å for all temperatures within the experimental error.

Using the experimental diffusion data of McCool and Woolf,²³ D. Chandler²⁴ established the temperature dependence of the hard sphere diameter of CCl₄. For 298 K he found 5.25 Å, for 323 K 5.23 Å, and for 348 K 5.20 Å.

Although the absolute value for σ_{CCl_4} of this paper (5.24 ± 0.05 Å) agrees well with the value for σ_{CCl_4} calculated by D. Chandler, unfortunately the change in

σ_{CCl_4} (0.05 Å) because of the temperature dependence is too small to be detected from our experimental data (error of σ_{HS} : ± 0.05 Å).

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