

Brillouin Scattering in Liquid Benzene Under High Pressure

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Brillouin spectra have been measured in liquid Benzene at high pressures up to 1300 bar and at the temperatures 298.15 K, 313.15 K, 323.15 K, and 343.15 K. From the experimental spectra the hypersonic velocities and the energy relaxation times were determined. The total velocity dispersion v_{∞}^2/v_0^2 due to the relaxation of the vibrational specific heat c_v is found to be nearly density independent in the pressure interval under study. It follows further that the experimentally determined specific heat corresponds to the theoretical value calculated with the vibrational modes of the Benzene molecule. The energy relaxation time τ_1 connected with all vibrational modes but the lowest decreases with increasing density at constant temperature, at constant density τ_1 decreases with growing temperature.

The relative relaxation rates were used to test the cell model (CM) with movable walls and the collision theory (HS) of Einwohner and Alder. Using a hard sphere diameter derived from experimental transport coefficients the experimental results were predicted better by HS than by CM.

Introduction

Information about vibrational relaxation in molecular liquids is obtained when the effects of temperature and density can be separated and both temperature and density are varied independently, since the effective hard sphere collision numbers change rather rapidly with only small variations of the density in liquids.

Light scattering experiments in liquids under high pressures allow measurements of the vibrational relaxation time as a function of density at constant temperature, where only the mean free path is changed in the liquid, and also measurements as a function of temperature at constant density, where mainly the transition probability between translational and vibrational degrees of freedom is changed.

There exist only a few Brillouin scattering measurements on liquids at high pressure [1–5].

Several workers have studied the vibrational relaxation of benzene in the gaseous and liquid states at atmospheric pressure, using ultrasonic and hyper-

sonic methods [6–18] and proposing various interpretations:

O'Connor and Schlupf [6] have determined the hypersonic velocity and the Landau Placzek ratio as a function of temperature and explained their data by a single vibrational relaxation process. Sorem and Schawlow [7] have measured also the sound velocity dispersion, using Brillouin scattering, and have explained their results by considering a single relaxation process involving the entire vibrational specific heat.

Hunter et al. [8] have made ultrasonic absorption and velocity measurements and have determined the hypersonic velocity by means of stimulated Brillouin scattering. They concluded that the vibrational specific heat associated with all but the lowest vibrational mode relaxes in the ultrasonic range while a second relaxation step, associated with the lowest vibrational mode, exists in the hypersonic range.

From spontaneous Brillouin scattering data Nichols et al. [9] were able to extract two relaxation times: $\tau_{v1} = 298$ ps and $\tau_{v2} = 36$ ps. Lucas, Jackson and Pentecost [10] calculated from their light scattering data a relaxation time $\tau_{v2} = 25$ ps of the lowest vibrational mode and a relaxation time $\tau_{v1} = 200$ ps of the rest of the vibrational modes. Hunter,

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Nichols and Haus [11] measured the ultrasonic absorption over the frequency range from 30 to 1000 MHz and deduced from their data two vibrational relaxation times in agreement with their earlier work [8, 9]. Ultrasonic and hypersonic measurements on liquid benzene of Takagi et al. [12] yielded the same result.

At high pressures, up to 1000 bar, Stith et al. [1] measured the hypersonic velocity of liquid benzene by means of stimulated Brillouin scattering, concluding that "... complete vibrational relaxation does not take place above pressures of 400 bars. This result is reasonable in terms of a double relaxation theory in that only a modest increase in the higher relaxation frequency is required."

Medina and Shea [4] have obtained Brillouin spectra from liquid benzene at temperatures ranging from 298 to 349 K and at pressures up to 3 kbar. They deduced from their hypersonic velocity data that complete vibrational relaxation takes place also at high pressures.

Unfortunately in both papers [1, 4] the hypersonic velocities were determined by using the simple Bragg formula for the frequency shift of the incident laser light frequency, a procedure which can lead to systematic errors of several percent in the value of the hypersonic velocity of relaxing liquids [19]. This error can lead to erroneous data for the relaxing vibrational specific heat. Data evaluation through computer fitting of theoretical spectra to experimental ones can avoid this error.

It was the first goal of this paper to decide whether the experimental relaxing specific heat was pressure dependent in the pressure range studied

A more detailed study on vibrational energy exchange must not only consider the macroscopically observable changes of the sound propagation properties of the liquid, but also the microscopic dynamics, which causes them.

Vibrational energy changes with sufficiently large amplitudes can be treated successfully with binary collision models [20]. A further argument for this procedure is given by a recent molecular dynamics study [21] on liquid Carbon tetrachloride at room temperature and at atmospheric pressure, that shows that the mean number of ternary collisions is about only 0.01 times the number of binary collisions. Therefore it may be justified to consider only binary collisions between molecules to be mainly responsible for the energy exchange between trans-

lational and vibrational degrees of freedom. In this case, the energy relaxation time can be factorized into the mean time τ_{BC} between collisions (corresponds to the inverse collision rate) and the inverse transition probability P per collision.

If the energy relaxation time is measured as a function of density at a single temperature, then relative relaxation rates can be derived by dividing the rate at high density by that at a lower reference density. If it is assumed that the transition probability P is independent of density [22], P drops out and collision models for the liquid state may be tested. τ_{BC} can be calculated from a cell model with movable walls [23] or from the collision theory of Einwohner and Alder [24, 25].

For the calculation of τ_{BC} with the aid of both formulas the knowledge of the effective hard sphere diameter of the molecule under consideration is necessary.

Parkhurst and Jonas have measured the effect of density and temperature on self-diffusion [26] and viscosity [27] and have derived from their data a temperature dependent effective hard core diameter of the Benzene molecule $\sigma = 5.12 \text{ \AA}$ at 303 K and $\sigma = 5.10 \text{ \AA}$ at 348 K in the framework of the rough hard sphere model [28].

The further goals of this paper were to check whether the double relaxing theory for liquid benzene is consistent with the total information accessible from Brillouin scattering involving not only the hypersound velocity but also the energy relaxation times.

By calculating the mean time τ_{BC} between collisions as function of density and temperature using the effective hard sphere diameter, given by Parkhurst and Jonas [26, 27], with the aid of the cell model [23], and the theory of Einwohner and Alder [24], it is possible to predict the ratio of the relaxation times at different densities as a function of density and therefore to examine these models for calculating collision rates in molecular liquids.

Experimental

An argon ion laser (Spectra Physics Model-165) in single mode operation ($\lambda = 514.5 \text{ nm}$) with a power of 150 mW was used as the light source for the measurements. The liquid benzene (Uvasol of fluorescence spectroscopy quality by Merck) was contained in a high pressure cell with three

windows in a 90 degree scattering geometry described previously [5].

The high pressure cell was surrounded by a thermostat to hold the temperature of the liquid sample constant within ± 0.2 K. The scattering angle was measured to be $90^\circ 20'$. The high pressure system consisted of a hand pump up to 700 bar and a hand screw press up to 2000 bar and a special fluid divider to transmit pressure from the pumping oil to the liquid under investigation without contamination of the sample. 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 stabilized five-pass Fabry-Perot interferometer with a free spectral range $\text{FSR} = 15.65$ GHz. During the experiment a finesse $F = 35-40$ was maintained. The scattered light signal was detected by a cooled photomultiplier with a dark counting rate of three counts per second and stored in a multichannel analyzer (MCA), which allowed the multiple scanning necessary for an acceptable signal-to-noise ratio. The MCA was triggered by the Rayleigh line to avoid broadening of the spectral components of the Brillouin spectra that results from drifts of the laser frequency relative to the interferometer pass frequency.

Results and Discussion

The hypersound velocities and the relaxation times were determined from each experimental Brillouin spectrum by fitting theoretical Brillouin spectra to it, considering the influence of the instrumental halfwidth of the Fabry-Perot interferometer. For the fitting procedure Mountains theory based on the relaxing bulk viscosity [29] was used for an effective single relaxation time and the extension for two relaxation times by Nichols and Carome [19]. A PDP 11/34 computer was used for these numerical calculations. The following pressure dependent data were taken or derived from the literature, necessary for calculating the theoretical Brillouin spectra: sound velocity v_0 at the limit of low frequencies [30, 31, 32], thermal conductivity [33], refractive index [34], shear viscosity [35], density ρ [26, 27, 36, 37]. The conventional method for computing the pressure dependence of c_p and c_v is based on the coefficient of thermal expansion and the isothermal com-

pressibility as derived from density measurements. However, in the case of liquid Benzene these data are not reliable enough, therefore another approach for calculating the pressure dependence of the specific heats had to be used [38]. The procedure, which was finally chosen, starts from the isothermal compressibility and the thermal expansion at atmospheric pressure and calculates the pressure dependence of the corresponding data by making use of the pressure dependence of the sound velocity. For further details see Sedlacek and Woehrl [38a]. Over a pressure range of 1000 bar the decrease of c_p is 4%, whereas c_v increases by the same amount. The pressure dependence of the ultrasonic damping α/f^2 was then calculated using the ratio α_p/α_0 as a function of pressure, given by Mifsud and Nolle [39] and the following values of α/f^2 at atmospheric pressure:

T [K]	298.15	313.15	323.15	343.15
$\alpha/f^2 \cdot 10^{17} [\text{cm}^{-1} \cdot \text{s}^{-2}]$	932	1007	1051	1194

These data were measured with the aid of an ultrasonic interferometer which allows the simultaneous determination of sound velocity (error $\pm 0.1\%$) and sound attenuation (error $\pm 3\%$) in liquids described previously [40]. For the nonrelaxing bulk viscosity, the corresponding values of the shear viscosity were taken [41].

This vibrational contribution to the sound absorption in the limit of low frequencies decreases with pressure: a fact, for which mainly the ratio τ_E/v_0 is responsible. (τ_E decreases with pressure, v_0 raises with pressure.) For an effective single vibrational relaxation time τ_E the absorption may be written [42]:

$$\alpha/f^2 = 2\pi^2 c_i (\gamma - 1) \tau_E / c_p v_0, \quad (1)$$

where c_p is the specific heat at constant pressure, γ the ratio of the specific heats at constant pressure and at constant volume, and c_i is the relaxing specific heat.

Figure 1 shows the effective single relaxation times, calculated with Eq. (1) (full lines), taking for c_i a theoretical value, which was calculated by means of all vibrational modes of the Benzene molecule, given by Shimanouchi [43], and the experimental relaxation times, using the computer fitting procedure, for two temperatures, $T =$

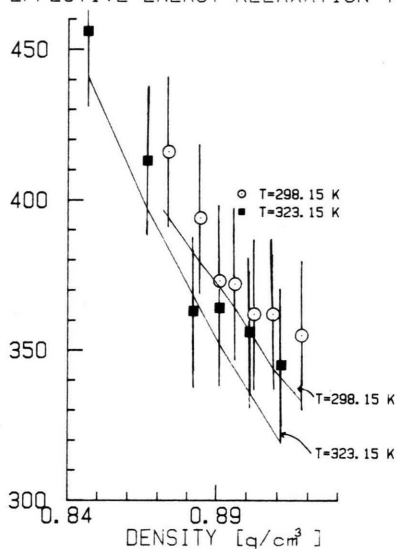
EFFECTIVE ENERGY RELAXATION TIME τ_E [ps]

Fig. 1. The effective energy relaxation times as a function of density. The full lines are the theoretical values of τ_E calculated with equation (1). Within the experimental error the experimental points correspond to theory, indicating that the relaxing specific heat is equal to that calculated with the aid of the vibrational frequencies of the Benzene molecule.

298.15 K and 323.15 K respectively. Within the limits of error it is shown, that the experimental points are corresponding to the value calculated with the aid of (1), indicating that the experimentally determined relaxing specific heat corresponds to the total vibrational specific heat calculated with the aid of spectroscopic data.

As the relaxation frequency $f_R = 1/(2\pi\tau_v)$ is small against the Brillouin sound frequency, the hypersound velocities can be taken for the sound velocities in the limit of high sound frequency with an error of 0.4%, which corresponds to the experimental error. The dispersion v_∞^2/v_0^2 is connected directly to the relaxing specific heat c_i :

$$v_\infty^2/v_0^2 = c_v(c_p - c_i)/(c_p(c_v - c_i)). \quad (2)$$

Figure 2 shows the hypersound velocities derived from the experimental Brillouin spectra at the four measured temperatures, the data of Stith at 300.15 K and the data of Medina and Shea. At nearly all temperatures in consideration our measured velocities are in agreement with the data of Medina and Shea (full lines), indicating that com-

plete vibrational relaxation takes place over the whole pressure range, in contradiction to Stith et al. [1] who interpreted the pressure dependence of their hypersound velocity data by assuming that at high pressures the vibrational specific heat does not relax completely.

Since high pressure light scattering cells are usually available only with three or four windows, the wave vector cannot be changed easily. At high pressure experiments therefore it is impossible to derive dispersion plots from which two vibrational relaxation times of liquid benzene could be separated directly. The evaluation of both relaxation times from one single Brillouin spectrum must therefore be based on the assumption that at high pressures the lower relaxation time corresponds to the lowest vibrational mode, and the higher relaxation time is adequate to all modes but the lowest, as found at atmospheric pressure [8–12]. Then more sophisticated evaluation of the experimental Brillouin spectra can be performed by using Mountain's theory of a double relaxing bulk viscosity η_B [19]. One part of η_B corresponds to the vibrational specific heat c_2 of the lowest mode, the other is

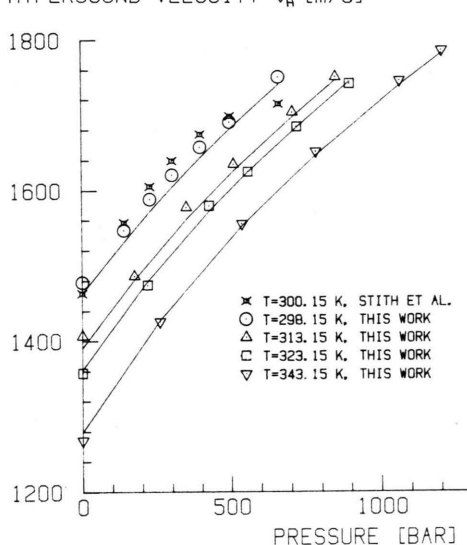
HYPERSOUND VELOCITY v_H [m/s]

Fig. 2. The hypersound velocities derived from experiment as a function of pressure. The experimental points of this work are in agreement with the data of Medina and Shea, indicating, that complete vibrational relaxation takes place over the pressure range studied, in contradiction to Stith et al.

equivalent to the specific heat c_1 of all the other modes of the Benzene molecule.

The corresponding relaxation times τ_1 and τ_2 , calculated as mentioned before, are shown in Fig. 3 as a function of density. At constant temperature τ_1 decreases with increasing density. This is due to the fact that with increasing density the mean distance of the molecules is decreasing and therefore the collision number is raising. As the transition probability is density independent in first approximation [22, 23], this effects a lowering of the relaxation time.

From Fig. 3 also follows that at constant density τ_1 decreases with increasing temperature. This can be explained with the temperature dependence of the transition probability [44, 45] and the thermal velocity, since at constant density the mean distance between the molecules remains almost unchanged. In measuring relaxation times as a function of temperature in a usually performed Brillouin scattering experiment this effect may be cancelled by the increase of the mean distance of the molecules with increasing temperature, which lowers the relaxation rate, while the growing transition probability increases the relaxation rate.

The relaxation time τ_2 , which corresponds to the lowest mode, is about 50 ps and nearly independent of density, but the scatter of the data is too large for drawing reliable conclusions. Therefore only the relaxation time τ_1 is used to test models for collision rates in molecular liquids. This can be done, since the relaxation time is directly proportional to the time between collisions τ_{BC} . (τ_{BC} corresponds to the inverse collision rate.)

This time between collisions τ_{BC} can be calculated with the aid of the cell model with "movable walls" [23]. τ_{BC} is predicted to be

$$\tau_{BC} = (d - \sigma)/v_T, \quad (3)$$

where $v_T = (8RT/\pi M)^{1/2}$ is the average molecular velocity and M is the molecular weight. X-ray measurements [46, 47] have shown that the average molecular arrangement in liquid Benzene is similar to that of the solid and indicate a tendency toward face centered cubic molecular packing.

$d = 2^{1/6} \left(\frac{M}{N \cdot \rho} \right)^{1/3}$ is the nearest neighbor distance

for the face centered cubic lattice. N is Avogadro's constant, σ is the effective molecular hard sphere

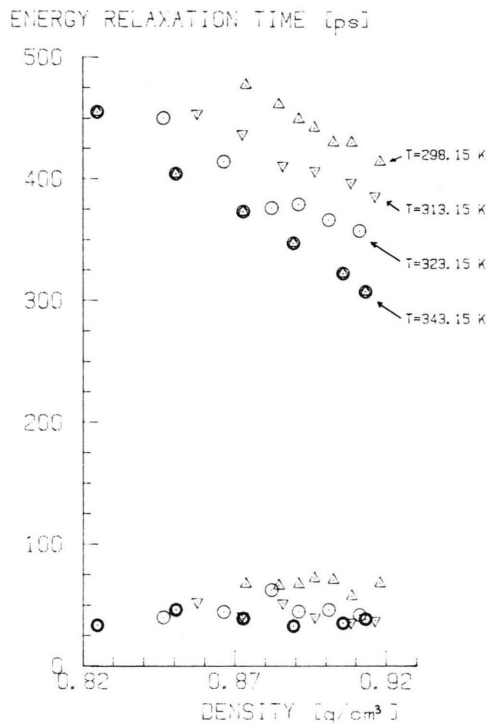


Fig. 3. The energy relaxation times τ_1 , corresponding to all modes but the lowest, and τ_2 , corresponding to the lowest mode as a function of density. τ_1 decreases with increasing density at constant temperature, and decreases with increasing temperature at constant density.

collision diameter. $d - \sigma$ is therefore the mean free path in the liquid. The cell model is appropriate to describe collision rates in dense gases and liquids, but is not applicable to gases at low densities when a particle is not effectively trapped in a cage.

Using the theory of Einwohner and Alder [24], where the collision rate at any density is shown to be the product of the dilute gas collision rate and the radial pair distribution function $g(r)$ at $r = \sigma$, the collision rate \tilde{N} can be obtained by (4):

$$\tilde{N} = \sqrt{2} \pi v_T N \rho \sigma^2 g(\sigma)/M, \quad (4)$$

where N is Avogadro's number and $g(\sigma)$ is the pair distribution function of two hard spheres of diameter σ in contact, which can be computed from the Carnahan and Starling formula [48].

From a theoretical comparison of the frequency of binary collisions as obtained from hard sphere molecular dynamics (Einwohner and Alder [24]) in

a liquid with that from the cell model [23] with movable walls follows [49]:

- 1) the density dependence of the collision rate is accurate in the region of high densities,
- 2) the temperature dependence is approximately correct,
- 3) the absolute value for the collision rate is in agreement with the Einwohner and Alder theory within a factor between 2 and 3.

For testing the different collision models on the basis of the experimental results, it is advantageous, as mentioned in the introduction, to consider only relative relaxation rates, since then the unknown transition probability drops out and relative collision rates, calculated from theoretical models, can be compared directly with the experimental results.

Even if only relative rates are compared, the knowledge of an absolute equivalent hard sphere diameter of the Benzene molecule is necessary for

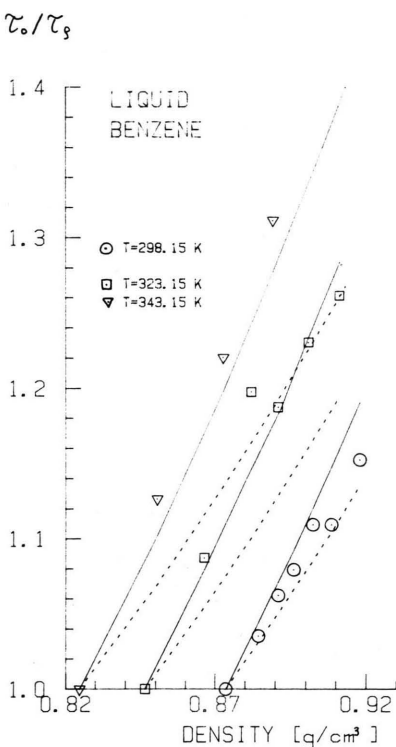


Fig. 4. Liquid Benzene: The ratio of the relaxation time at atmospheric pressure and the relaxation time at different densities as function of density. The collision model of Einwohner and Alder (full line) fits the experimental points better than the cell model (dashed line).

τ_0/τ_g

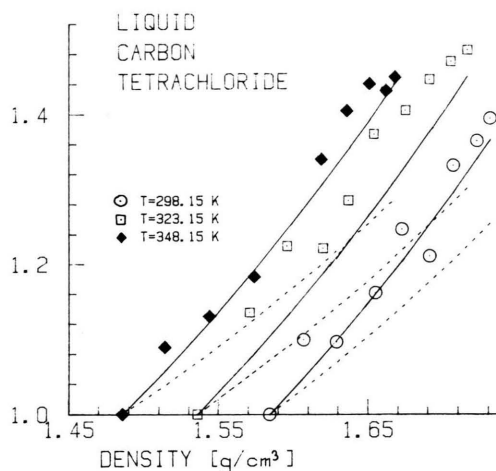


Fig. 5. Liquid Carbon tetrachloride: The ratio of the relaxation time at atmospheric pressure and different densities as function of density. Again, the collision model of Einwohner and Alder (full line) fits the experimental points better than the cell model (dashed line).

the calculation of the time between collisions in both models (cell model and model of Einwohner and Alder). For the vibrational relaxation mechanism collisions with high energy are more important than those with low energy, since only an encounter with enough energy can effect a change of the quantum states of the molecules. Therefore one is led to assume that an appropriate molecular collision diameter for the description of vibrational relaxation mechanism may be smaller than a hard sphere diameter, which is derived from experimental transport coefficients where soft and hard collisions are counted with equal weight.

Keeping this fact in mind, theoretical relative collision rates were calculated on the basis of both models with a temperature dependent hard sphere diameter ($\sigma = 5.12 \text{ \AA}$ at 303 K and $\sigma = 5.10 \text{ \AA}$ at 348 K) derived from transport coefficients (shear viscosity and selfdiffusion) by Parkhurst and Jonas [26, 27]. Surprisingly it is found, as Fig. 4 shows, that the slope of the collision model of Einwohner and Alder (full line) is in agreement within the experimental error with the data points of this experiment. This result may indicate that even the model of Einwohner and Alder might not predict the collision rates correctly, since a realistic collision diameter, as mentioned above, should be smaller than

that derived from transport coefficients. The slope following from the cell model (dashed line) does not correspond to the experimental points, and would only agree with experiment if a larger hard sphere diameter would be used; this makes the applicability of the cell model more improbable.

This discrepancy between the two models could be a more common phenomenon, as an analogous result for Carbon tetrachloride shows (Figure 5). Here also a hard sphere diameter of 5.25 Å, derived from transport coefficients by Chandler [28], was used in calculating the relative collision rates of both

models. Again, the model of Einwohner and Alder gives a reasonably good fit to the experimental data, in contrast to the slope derived from cell model.

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