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Abnormal temperature-dependent variation in sound velocity for the molecular liquids benzene and hexafluorobenzene

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In this paper we give the results of sound-velocity measurements by accurate Brillouin techniques in pure liquid benzene and hexafluorobenzene in the temperature range 20–60 °C. For both fluids, we find a clear change in the slope of the variation of the sound velocity with temperature. A change in the Landau-Placzek ratio was also detected. These experimental facts seem to confirm that a molecular-orientation ordering change occurs in this temperature range for these fluids. We see some similarity in these velocity changes with previous results found for phase changes in fluids. We believe that when the dominant molecular orientation changes in a local order scale, it creates a process strong enough to perturb the hydrodynamic behavior of the fluid, which can then be detected by spontaneous Brillouin light scattering.

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I. INTRODUCTION

Liquid-structure studies were developed many years ago with different techniques, such as light scattering [1], neutron scattering [2–5], and x-ray diffusion [2,3,6]. This tremendous amount of effort was mainly devoted to the determination of the interaction between molecules and the explanation of the intermolecular configuration of molecular liquids.

In aromatic liquids, it is well known that the structure of, e.g., benzene is not easy to describe with known potentials, but detailed experiences in neutron scattering and x-ray diffraction at room temperature in a pure fluid and mixtures with hexafluorobenzene gave some interesting information about the dominant configuration of pairs of molecules [the so-called T (two perpendicular in a letter T form), L (two perpendicular shifted molecules in a letter L form), and stack configurations] and the origin of the forces acting in the fluid. For example, the work of Bartsch and co-workers [2,3] shows that the quadrupolar forces are responsible for the local molecular "structure" of benzene, hexafluorobenzene, and their mixtures, instead of the packing effects.

Other studies were developed for the understanding of the dipole interaction in aromatic liquids for different permanent dipole moments [4]. In these experiences, the temperature dependence was chosen to check the liquid structure in the vicinity of the solid-liquid transition temperature and for increasing temperature deviation in the liquid side.

New results obtained in temperature change of specific heat [7,8] and depolarized-light scattering [8] seems to us in Bordeaux important enough to start a study of the static and dynamic changes of these fluids with a temperature variation. We decided to start full dynamic-structure-factor studies in our laboratory because we have experience in Rayleigh-Brillouin studies of both gases and liquid fluids.

Studies devoted to thermodynamic properties of benzene in the temperature range of 20–60 °C, started in St. Petersburg a few years ago [7], and interesting new results were obtained, among other methods, by depolarized-light-scattering techniques. In this paper we first summarize previous works devoted to thermodynamic and structure knowledge of pure liquids. We then present experimental results obtained by Brillouin position measurements in benzene and hexafluorobenzene liquids in the temperature range just defined. We also interpret our results, after showing that the sound-velocity behavior is similar to that of liquids with big correlation lengths (such as in situations corresponding to the phase-transition theory).

As established by the temperature-dependent measurements of heat capacity, at 35 °C some characteristic change occurs, giving the appearance of the possibility of the beginning of some process of "ordering" change in the fluid. This change in the order can be assumed as the beginning appearance of a different local structure in the fluid.

Measurements of benzene seems to show that there are possibilities of the determination of different values of the orientation pair-correlation function, as determined by numerical simulation by Steihausser [9].

In the framework of that kind of study, we decided to explore the sound velocity of benzene and hexafluorobenzene in the temperature region of interest. We present here the results obtained with the experimental setup developed in Bordeaux, but some points obtained in St. Petersburg are essentially in agreement with those obtained in Bordeaux.

II. EXPERIMENT

The experimental setup is similar to the setup used and described in Ref. [10], but we added a thermalization system to be able to scan the temperature range 15–75 °C with a temperature stability of at least 0.01 °C (the room temperature is stabilized at roughly 0.1 °C, at least during the accumulation of the spectrum of each experience), and we did not detect any temperature variation of the thermal bath of the sample. We used a numerical thermometer with two calibrated platinum resistance detectors, giving measurements of a precision of 0.01 °C. Two energy sources heat the sample. The first allows the system to be warmed up to a desired temperature and the second allows its stabilization to the required value.

The hexafluorobenzene was prepared in St. Petersburg and the sample was stored in a different cell from that used in Bordeaux; the sample was the same that the one studied in Ref. [1(b)].

The benzene sample which was prepared in Bordeaux was stored in a sealed assay tube after triple distillation under vacuum, after a previous careful elimination of dissolved gases, until we were virtually sure that the liquid was in equilibrium with its saturated vapor. The dissolved gases are eliminated by pumping the volume of the cell after the liquid is frozen. The cell is then insulated and the liquid state recovered by slow heating. A new freezing is then effected and we pump again in the cell. One can find a large amount of bubbles at the first freezing cycles (the return to room temperature is realized by exchange with a warm source, to avoid confusion with bubbles coming from possible boiling). This shows that there is a significant amount of dissolved gases, even if the distillation is effected under a good vacuum. The elimination of dissolved gases is an important aspect of purification of a good solvent, such as benzene.

The sample is placed in the center of a cylindrical container. This container is filled with a fluid for an homogeneous temperature. The cylindrical container with a set of two parallel windows is thermally insulated by a structure made with polyurethane.

The optical devices are placed on a marble table, which is mechanically insulated from the vibrations of the building. A Spectra Physics 2020 argon laser delivers a monomode radiation and we use the 5145-Å radiation. The scattered light is analyzed with a double-pass plane Fabry-Pérot interferometer that is piezoelectrically scanned. We search and control the parallelism with a device built in the laboratory [11]. Both the laser and the Fabry-Pérot interferometer are mechanically insulated from the marble tale, in order to eliminate transmission of jitter vibrations of the head of the laser to optics, primarily the double-pass Fabry-Pérot interferometer. Each run, corresponding to the 1024 points of the multichannel analyzer (MCA), of the piezoelectric plates of the Fabry-Pérot interferometer is decomposed by two choppers into two different parts.

The first 200 points describe the apparatus function, centered in the 100th channel. During this step the probe beam is stopped by the first chopper. The other points between 201 and 1024 gives the scattered spectrum, and the alignment beam is stopped by the second chopper, which is placed in front of the alignment beam. During a short period both beams are stopped to evaluate the dark current of the photomultiplier and to obtain the electric zero level. The apparatus function, the free spectral range (FSR), the photomultiplier noise (electronic zero), and the dynamic structure factor (with a good signal-to-noise ratio) is then obtained. The FSR can take any value corresponding to the Fabry-Pérot optical-plate separation between 0.01 and 150 mm. For that study we chose values corresponding to 25 000, 17 000, and 9375 MHz.

III. RESULTS AND DISCUSSION

In our experiments, we study the full Rayleigh-Brillouin spectrum and particularly (1) the position of the Brillouin line, (2) the intensity ratio between central lines and shifted lines and their width for a variation of the temperature between 18 and 60 °C. The spectra analysis is based on a full dynamic-structure-factor $S(q,\omega)$ description. For this purpose we simulate a spectrum with a central thermal mode (and for benzene a bulk viscosity relaxation mode introduced by Mountain [12]) and two shifted sound modes with their antisymmetric component. It must be noted that optical adaptation of the hexafluorobenzene cell gives spectra of lesser quality than the benzene cell, and we do not obtain the same accuracy as in benzene experiences.

We convolute this calculated factor with the experimental apparatus function. We point out that our apparatus function is that obtained by the accumulation of the apparatus functions of each scan and is therefore the true mean apparatus function (the number of accumulations of 0.7 s is always bigger than 2000 so that we have more than 1.4 s of accumulation per point).

We can say that the precision of our spectroscopic measurements meet the requirements given by Vaughan in his fundamental contribution to the knowledge of the Fabry-Pérot interferometer [12]. Using Vaughan's method, the high flux and amount of information leaves an estimated precision of 0.24%, smaller than the 0.6% of our work.

We have an apparatus function for each spectrum, with an equivalent average than the scattered spectrum. The FSR can be adjusted for each fluid we studied or line of interest, but we decided to set the Brillouin line close to one-third of the FSR, in order to minimize overlapping effects. Typical finesse is 40, but the knowledge of the "true" finesse of the experiment allows us to evaluate the theoretical spectra in a realistic way when we calculate convoluted spectra. The precision of the sound velocity is 0.6%, which is a usual value for the adjustment of a broad line such as the Brillouin spectra of a liquid. The measurement of the Brillouin width is less precise because the exact knowledge of the depolarized background is needed. The simulation is effected with an apparatus function several times sharper than the Brillouin line so that the full description of the spectrum can be obtained.

The central mode is in good agreement with previous works, and the thermal diffusivity mode $D_T q^2$, where $D_T = \lambda/\rho C_P$, associated with a mountain mode follows the expected temperature variation in the limits of our experimental resolution. We are able to evaluate the thermal evolution of the mountain line. As expected, because this mode is connected to internal molecular modes, nothing special happens to that line and an exponential temperature dependence is found, but this analysis is outside the scope of this paper. An unusual Landau-Placzek ratio found for benzene seems to show that some unresolved small contribution appears in the central part of the spectrum for the same temperatures when the velocity reaches a minimum. The sound velocity value is obtained when the full spectra is correctly described.

Let us point out that the previously detected frequency-dependent change of the benzene Brillouin position (corresponding to the relaxation between hypersonic and ultrasonic velocity) is outside our experimental domain [13]. This ensures that we are analyzing a different physical phenomena: we are looking at a temperature-dependent change, instead of a wave-vector-dependent dispersion.

In Figs. 1 and 2 we plot the sound velocity of, respectively, benzene and hexafluorobenzene for different temperatures. In Fig. 3 we show the temperature variation of the Landau-Placzek ratio for benzene.

For both fluids, a normal monotonically decreasing behavior of the sound speed is observed in the temperature range 20–30 °C. The general behavior roughly corresponds to the usual decreasing of the sound velocity with increasing temperature and when a phase transition is approached and crossed [14].

Between 33 and 51 °C, we see a dramatic change in the slope of the sound velocity. Above 51 °C the velocity decreases with a monotonic slope which seems almost different from the initial value. In this temperature range, one sees a decrease over a few degrees, then a rapid increase, followed by a rapid decreasing. The last slope changes around 52 °C; the slope joins a value not too different from the one before 30 °C. It is very interesting to note that the two fluids change their slopes of variation of the sound velocity roughly for the same set of temperatures, but the speed values are very different, according to the approximate mass-dependent variation defined by $M^{-1/2}$ [15]. The value of the velocity changes from 1485 $\mathrm{m\,s^{-1}}$ for benzene to 850 $\mathrm{m\,s^{-1}}$ for hexafluorobenzene at 20 °C, as a mass effect in the velocity of those two molecules; because similar quadrupole forces play a role in the local molecular liquid structure of those symmetric molecules, it is not surprising to have molecular liquid-structural changes for the same range of temperatures. This point has to be connected to the fact that the known structure of the molecular fluid is concerned essentially with the electrostatic forces, and not with packing effects [2,3].

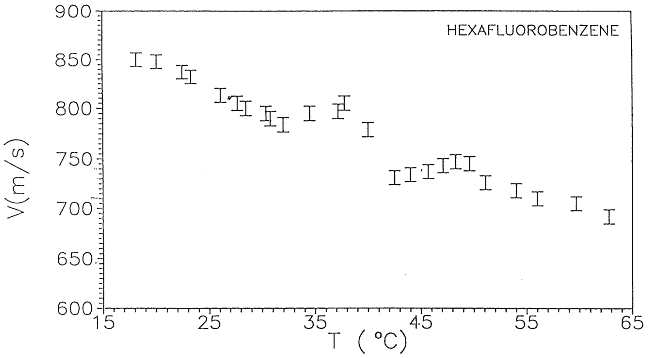

FIG. 2. Temperature dependence of sound velocity of hexafluorobenzene.

In Fig. 3, we see that the Landau-Placzek ratio increases with temperature as usual, but there are two extra maxima obtained for the temperatures corresponding to a minimum value of the velocity. This result means that there are two temperature ranges where some new undetected energy is centered in temperatures of minimum of velocity. This amount is small and probably not resolved by the technique we used. This increase of the central intensity is similar to the behavior of a mode with a slow characteristic time, and with some crossover between molecular local reorientation of molecular orientation of liquid structures and the hydrodynamic behavior of the fluid.

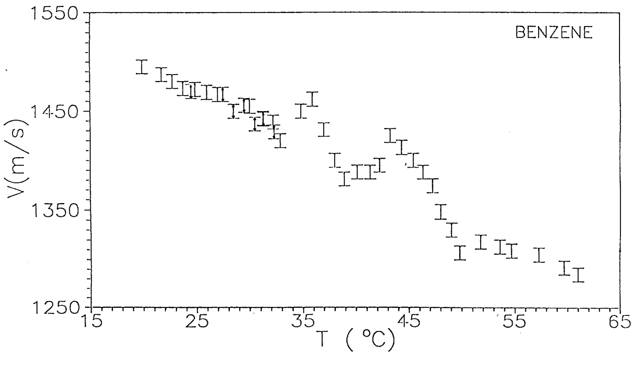

FIG. 1. Temperature dependence of sound velocity of benzene. Extra points in low-temperature region, denoted by double arrows, correspond to experiments effected at St. Peterburg.

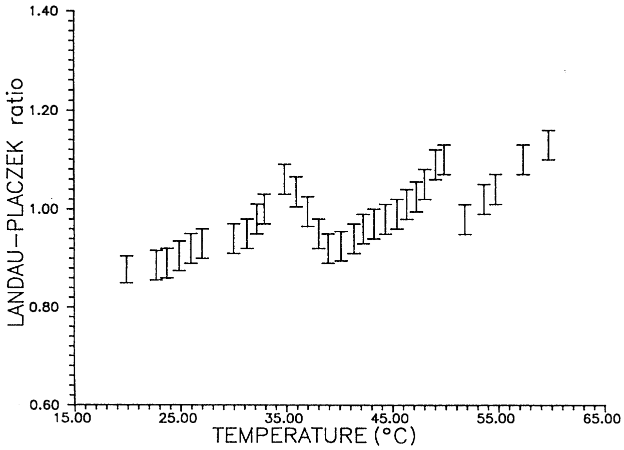

FIG. 3. Temperature variation of Landau-Placzek ratio of benzene.

As mentioned above, both molecules are known for their strong and *similar but opposite sign* quadrupole moment Q_m, $Q_{m\mathrm{B}}=(-29.0\pm1.7)\times10^{-40}$ m^2 for benzene and $Q_{m\mathrm{HFB}}=(31.0\pm1.7)\times10^{-40}$ m^2 for hexafluorobenzene [1]. For this reason, these two fluids are usually studied together, for example, for the investigation of the structure of molecular liquids. Quite close solid-liquid and liquid-gas temperature transition, and equivalent molecular symmetry and absolute value of the quadrupolar moments, seems to lead to orientation structure changes for the same range of temperatures.

If we look at the details of the sound velocity oscillations with temperature, we see that for benzene it decreases smoothly until a value roughly equal to 34 °C. Then it increases to a first maximum close to 36 °C, followed by a rapid reduction to 39.5 °C. A second oscillation starts after this temperature with a rapid growth until 43 °C and a decreasing which reaches a small minimum at 50 °C. After 50 °C, for the last experimental points, the variation of the velocity is smooth again. Let us also point out that the two rapidly decreasing regions correspond to velocity changes of, respectively, 90 and 120 m s^{-1}.

Hexafluorobenzene sound-velocity changes are similar to those of benzene but, as expected, with different temperatures. The first minimum is at 33 °C and the first maximum at 38.5 °C (2.5 °C higher than that of benzene). The second minimum is at 42 °C and the last maximum at 49.5 °C. The last minimum is less pronounced than in benzene and is situated at a temperature close to 51 °C. Also, the changes in sound velocity of hexafluorobenzene are less pronounced than in benzene.

One possible explanation for our results can be expressed as follows. Light-scattering Rayleigh-Brillouin techniques give information for low frequencies about some collective behavior, coupled with a correlation of density fluctuations. We believe that small-structure fluctuations are uncoupled with Rayleigh-Brillouin spectra but, for some temperature, the change in the local structure affects a number of molecules big enough and fluctuations have a correlation length so big and intense that they perturb the hydrodynamic behavior of the molecular liquid.

Previous studies of hypersound velocity in liquids, especially in benzene, were performed with temperature intervals of several degrees [16] and probably without a careful elimination of dissolved gases. A small variation in temperature was developed for sound-velocity changes, only in systems supposed to change rapidly with temperature such as liquid mixture phase changes studied by Chen and Polonsky [14(b)] and Aref'ev and Fabelinskii [14(c)].

The change in the sound-velocity slope occurs in a temperature range limited by the change in the heat capacity for the lower temperature and the detected change in the depolarized intensity observed previously for the upper one [7,8]. In our opinion this fact shows that we are looking at the same phenomena.

It is interesting to note that, in benzene, the first minimum of the sound velocity is at almost the same temperature as the change of slope of the specific-heat variation with temperature. That is, as can be seen in previous works devoted to the sound-velocity measurements in fluids, a minimum for this property is detected for big perturbation crossing, such as the critical point [14(b), 14(c)], or in the critical density crossing during the study of an isothermal line [14(d)]. We see that the detected velocity reaches a minimum at the same temperature for which the specific-heat slope changes. This means that we have the behavior of a phase change for the velocity. In fact, the change is not simple and two change processes seem to happen in the fluid. Such behavior of the sound velocity was detected, for example, in Ref. [14(a)], where the drop in velocity was observed in the temperature range corresponding to the formation of liquid-crystal phase in the melts of dibenzyl and diphenyl (this aspect gives a connection with some organization of the fluid which changes with temperature, as in this medium).

Otherwise, for liquid mixtures, there is first an interesting result of velocity change for nitrobenzene–*n*-hexane mixture with a critical temperature $T_c=20.20\,^\circ\mathrm{C}$ with $x_c=0.42$ mole fraction of nitrobenzene in *n*-hexane found by Chen and Polonsky [14(b)]: the velocity slope changes and presents a minima when the temperature T_c is approached. A second result is given by Aref'ev and Fabelinskii [14(c)] for the measurement of the sound-velocity change for the crossing of the critical temperature $T_c=30.95\,^\circ\mathrm{C}$ of a 0.4 mole fraction of nitroethane-isooctane mixture. In this last experiment, the concentration central mode is small, which explains how the authors were able to measure the velocity on both sides of T_c. For that temperature, they obtain with a minimum of the sound velocity, with an equivalent to the behavior we found for each oscillation of the sound velocity in benzene and hexafluorobenzene. All these physical arguments give us enough understanding to try to interpret the results in the framework of some crossover between local molecular change of structure and hydrodynamic modes, presenting equivalent effects to those found for critical phenomena.

A possible theoretical framework for the interpretation of this kind of experimental results can be also found in the theoretical work of Mitus, Patashinskii, and Shumilo, devoted to the possibility of some kind of phase change in pure fluids between two different structures [17].

Recent papers on NMR and specific-heat studies in quinolin (with slope change happening at 17 °C) conducted by Jalabert *et al.* [18] and devoted to the study of the problem of structure changes in fluids with significant electrostatic forces seem to show that the change in the fluid local structure with temperature is a general phenomena when strong enough forces exist.

We plan to do a careful and accurate experimental study, and measure all the detectable effects of that phenomena in the dynamics of molecular liquids with strong electrostatic forces. Other techniques must be used for the study of this phenomena: x-ray diffraction, neutron diffraction, and NMR, as shown successfully by Jalabert *et al.* [18]. New encouraging results have been found in quinolin and quinolin derivatives for transport and thermodynamic coefficients [19].

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