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Anomalous effects in the temperature dependence of depolarized Rayleigh spectra of benzene and quinoline

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The temperature dependence of vertically (incident) and horizontally (scattered) depolarized spectra of benzene and quinoline has been very carefully investigated. For more confidence, in benzene, independent measurements with different techniques were performed both in Bordeaux and Messina. The reorientational correlation time shows an overall behavior equivalent to that previously reported when temperature varies by steps of the order of a few K. Anomalous behavior is, however, observed for both neat liquids at given very well reproducible temperatures when temperature varies by small steps. These temperatures may correspond to regions where molecular reorientation is slowed down. [S1063-651X(96)02211-8]

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I. INTRODUCTION

After the pioneering works of Rozhdestvenskaya and Smirnova [1], recent accurate measurements of the heat capacity [2], depolarized total scattered intensity [3], NMR relaxation time [2], hypersound velocity [4], Landau-Placzek ratio [4], dielectric relaxation [5], and neutron scattering [6] of both liquids benzene and quinoline show that clear ''accidents'' occur at some characteristic temperatures. For instance, a quantity which usually increases with temperature suddenly decreases at a given well reproducible temperature and then increases again. Such anomalies are only observed when great care is taken in the preparation of the sample: high chemical purity, almost complete degassing, very long thermal equilibrium times, and very slow heating or cooling rates. These unexpected behaviors presently have no clear physical interpretation and are outside the understanding of usual liquid theories. These experimental results, however, may be connected to those published by Fischer [7], who detected abnormal thermal behavior in glass forming liquids made by small molecules. In this latter case long range correlation lengths are measured whereas the thermodynamic state of the fluid is far from any critical point.

It is obvious that more experimental data using different techniques have to be obtained in order to suggest the directions where the theoretical investigations and the numerical simulations have to be developed.

In the framework of this experimental effort, we used depolarized dynamic light scattering, one of the nonperturbative experimental methods very well suited for the study of the molecular reorientations. This technique has already been used in numerous previous experiments [8]. In the present experimental study, we given results about the orientational correlation time τ deduced from the analysis of the vertically (V) (incident light polarized vertically), horizontally (H) (scattered light polarized horizontally) depolarized spectrum of the light scattered by benzene and quinoline, in a large temperature domain along the liquid-vapor coexistence curve. Two different experimental techniques have been used in Messina and in Bordeaux, respectively, a high-resolution grating spectrometer and a Fabry-Pérot interferometer. We will show that the correlation time τ has an anomalous behavior at the same temperatures as those previously reported by dielectric relaxation and neutron scattering [2,5,6].

II. EXPERIMENTAL SETUP AND RESULTS

The experimental procedure of the Bordeaux group is as follows. The sample is first filtered on a Millipore filter to remove dust particles, then triply distilled under vacuum and stored in a sealed Pyrex tube. The dissolved gases are eliminated by pumping the volume of the cell after the liquid is frozen at liquid nitrogen temperature. This operation is repeated at least two times and even though the distillation has been achieved under a good vacuum, a significant amount of unwanted dissolved gases is obtained. It has to be stressed that in order to obtain reproducible results, a very careful elimination of dissolved gases is an important aspect of the experimental procedure. The sample contained in a cylindrical Pyrex tube is embedded in a water bath whose temperature can vary in the range 15 °C–75 °C with a very long term stability better than ±0.005°C. The temperature is measured with an accuracy of ±0.001 K by using two calibrated platinum resistors connected to a high accuracy impedance bridge. After the temperature of the sample is set to the expected value, we wait a few hours before the depolarized spectra are recorded.

All the optical part of the setup is mounted on a heavy granite table insulated from the thermal vibration of the building. The sample is irradiated by the 0.5145 μm single frequency radiation vertically (V) or horizontally (H) polarized, emitted by a Spectra Physics 2020 Ar$^+$ laser. The scattered light at 90° is analyzed by a double-pass Fabry-Pérot

(FP) interferometer piezoelectrically scanned. The spacing between the two plates of the FP can be adjusted in a large domain. The FP is disposed in a temperature controlled chamber (±0.05°C) and the parallelism of its plates is automatically optimized during the experiment by using a device built in the laboratory [9]. Both the laser and the Fabry-Pérot interferometer are mechanically insulated from the granite table, in order to eliminate transmission of jitter vibrations of the head of the laser to optics, essentially the double-pass Fabry-Pérot interferometer. After crossing the FP interferometer, the scattered light is received on a photomultiplier connected to a multichannel analyzer (MCA) via a photon counter. Each run is divided in three parts by convenient choppers allowing simultaneous recording of the apparatus function, the spectrum, and the electrical zero level.

The group at Messina uses a double monochromator double pass (DMDP 2000) built by SOPRA, a French optical device company. This setup has been fully automated and details of optical arrangement can be found in [10]. Note again that it is a different spectroscopic method (monochromator instead of Fabry-Pérot interferometer) and a different deconvolution method since the instrumental function is almost a Gaussian with no overlapping of orders.

III. ANALYSIS OF THE EXPERIMENTAL RESULTS

Numerous theories concerning depolarized *VH* spectra can be found in the literature. Since the pioneering theoretical works of Leontovich [11], it is now admitted that the *VH* spectrum shows a fine structure associated with the coupling between the reorientational motion of the molecules and the vorticity of the fluid. Experimentally, besides a central Lorentzian line, the *VH* fine structure continuously evolves from two small side humps at low temperature, close to the glass transition temperature, to a ''shear dip'' at zero frequency at moderately low temperature and then to a ''normal'' Lorentzian behavior at high temperature. Many different formulas have been proposed to describe the shape of the *VH* spectrum and for the present analysis, we shall use the most recent one proposed by Quentrec [8] which is valid for dissipative shear waves, a regime pertinent for our experiments.

$$I_V^H(k,\omega)=\sin^2\frac{\theta}{2}\,\frac{\Gamma}{\omega^2+\Gamma^2}+\cos^2\frac{\theta}{2}\,\frac{\Gamma\left(\omega^2+\eta_0\eta_\infty\frac{k^4}{\rho}\right)}{\left(\omega^2-\eta_0\frac{\Gamma k^2}{\rho}\right)^2+\omega^2\left(\Gamma+\eta_\infty\frac{k^2}{\rho}\right)^2}. \tag{1}$$

In formula (1), ω is the frequency, k is the transfer wave vector, θ is the scattering angle, $\Gamma=1/\tau$ is the reorientational rate of molecules, τ being the reorientation time, ρ is the density, and η_0 and $\eta_\infty=\eta_0(1-R)$ are, respectively, the low and high frequency values of the shear viscosity. R is a coupling constant such as $0<R<1$. In most cases, R is about 0.4.

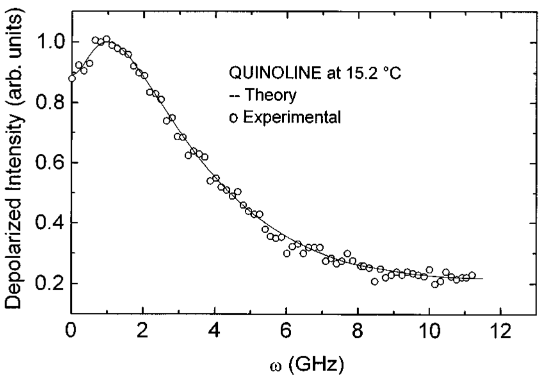

FIG. 1. Typical depolarized spectrum of quinoline. Note the ''shear deep'' at zero frequency and the good agreement with formula (1) of the text.

In addition to orientational motions, other phenomena such as librations and molecular collisions which induce anisotropy have to be taken into account. These two last phenomena occur at high frequency and will appear as a small flat background when analyzed with the Fabry-Pérot interferometer.

Experimental results have been analyzed in terms of formula (1) for both liquids. In the case of quinoline in the temperature range from 15 °C to 60 °C, the *VH* spectrum evolves from a fine structure with a ''shear deep'' at the top to a single Lorentzian. In the case of benzene when the rotational line is rather broad, we have been unable to put in evidence the fine structure. This may be due either to the relative value of $\Gamma\rho/\eta_0 k^2$ which is of the order of 40 for 90° scattering or to the smallness of the coupling constant R. One example of the depolarized spectrum of quinoline is shown in Fig. 1.

The most interesting result of the present analysis is the temperature variation of Γ. Whereas the natural tendency of the reorientational rate Γ is to increase when increasing temperature, we observe two detectable anomalies centered at temperatures close to 36 °C and 46 °C for benzene and 17 °C and 42 °C for quinoline as shown by Figs. 2 and 3. Note in Fig. 2 the nice agreement between points obtained in Bor-

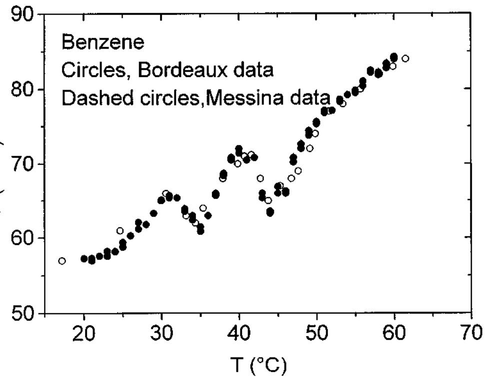

FIG. 2. Temperature change of depolarized reorientation line of benzene. Both Messina (monocromator) and Bordeaux (Fabry-Pérot) results are plotted. The almost full agreement of both measurements has to be quoted.

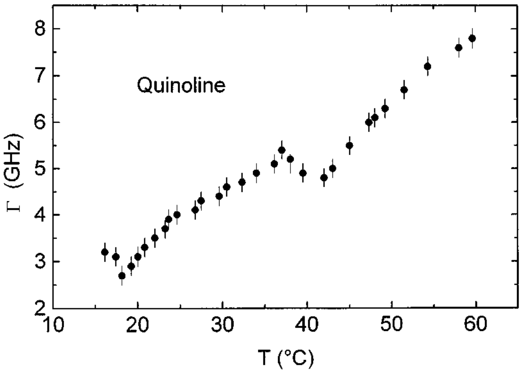

FIG. 3. Temperature change of depolarized reorientation line of quinoline.

deaux and those obtained in Messina. What is amazing is that these anomalies in Γ occur exactly at the same temperatures where abnormal behaviors of the velocity of sound and the Landau-Placzeck ratio in liquid benzene [4] and quinoline [5] were detected. The shear deep mode seems unaffected in the limits of our precision.

Another important parameter deduced from our experimental results is the depolarization factor, defined as the ratio between the total depolarized intensity I_V^H and the total polarized intensity I_V^V This factor can be measured by integrating on frequency the polarized *VV* and depolarized *VH* structure factors. In Figs. 4 and 5, the behavior of the depolarization factor versus temperature is represented, respectively, for benzene and quinoline. This depolarization factor presents an important oscillation centered for both fluids in the two particular temperatures.

IV. DISCUSSION

As said before, we roughly found that the behavior of the relaxation time of both fluids is in agreement with previous works, except for the small temperature range centered in the vicinity of two temperatures where an anomalous behavior is observed.

The activation energy of molecular reorientation has been evaluated for both liquids outside the two regions defined before, and leaves values of (2.74±0.15) kcal/mol for benzene and (3.65±0.15) kcal/mol for quinoline, equivalent to the values found by Jackson and Simicd-Glavanski [12], Enreight, Stageman, and Stoicheff [13], and others [14]. In the vicinity of the temperatures of the accidents, we can evaluate an extra energy. They are, respectively, (1.85±0.15) kcal/mol for benzene and (4.85±0.15) kcal/mol for quinoline. In the case of benzene, the values we obtained can be consistent with the activation energies proposed by Steinhauser [15] for the changes of orientational forms of benzene.

For quinoline, there is no available mechanism like the one proposed for benzene. Therefore more detailed numerical simulations and further experiments (such as the ones effectuated on benzene by Bertagnolli and co-workers [16]) are needed for a deeper analysis of this fluid.

The depolarization factor presents values of the same magnitude as those presented, for example, in [14], but an important perturbation is found in the vicinity of the temperatures where accidents have been reported for the reorientational linewidth. We have to recall that equilibrium is reached by waiting at least 4 h between steps of roughly 2 °C. The usual interpretation of a bigger depolarization factor can be attributed to a greater size of the scattering particles. This behavior is equivalent to the local ordering of scattering particles. In this case, the ‘‘cage effect’’ is enhanced and rotational diffusion slowed down.

The development of the study of liquids and supercooled liquids belonging to the class of glass forming liquids provides many results indicating that there are slow modes and long range correlations in liquids.

In the framework of this general idea, some theoretical approach can be used, as proposed by Thirumalai and Mountain [17] and Bagdassarian and Oxtoby [18] for coexistence of long range and short range correlations or coexistence of ergodic and nonergodic domains in fluids. More general models such as the mode coupling theory [19] and the percolation model of Tartaglia, Rouch, and Chen [20] are employed essentially in the field of glass forming liquids, but we are not sure that these models are pertinent approaches to explain our experimental results.

The connection of long time reorientations in ‘‘microemulsified’’ benzene and other glass forming liquids detected by Angell and co-workers [21] is an interesting method for the understanding of long time long range pro-

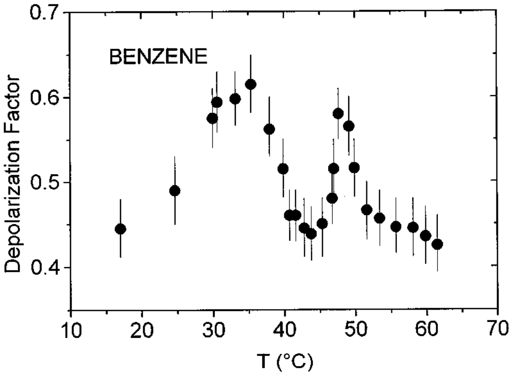

FIG. 4. Temperature change of depolarization factor I_H^V/I_V^V of benzene. Note that the oscillation is much bigger than error bars.

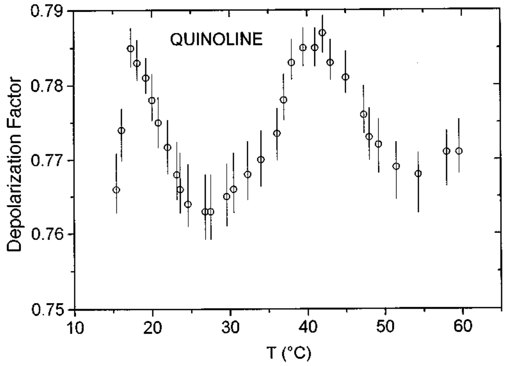

FIG. 5. Temperature change of depolarization factor I_H^V/I_V^V of quinoline.

cesses reported in this work. These authors claim that with ‘‘microemulsification’’ techniques, it is possible to measure liquid structural relaxation times of about 100 s.

Our results seem to show that the slowing down of the reorientation time is a different effect than the coupling between shear modes and reorientation. Then we can think, following Quentrec’s [8] hypothesis, that there are several unknown relaxation processes in viscous fluids or glass forming liquids. We therefore believe that the models of Kawasaki [22] and Kivelson and co-workers [23] very recently published could be extended in the future to provide a full understanding of this phenomenon.

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