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Asymmetry in the Brillouin spectra of organic fluids exposed to a temperature gradient

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We describe measurements of Brillouin intensity asymmetry induced by an applied temperature gradient in liquid samples characterized by a high derivative of the refractive index with respect to the temperature. We have used two liquids of distinct polar nature, benzene and isopropyl alcohol, and we have avoided finite-size and nonlinearity effects. The data are in good agreement with existing linear nonequilibrium statistical theories. The results suggest a general behavior of the effect in fluids, not related to their molecular structure.

The study of fluids out of equilibrium is of particular interest,[1–3] as they can be used as a probe to check statistical methods used in nonequilibrium physics. It is well known that when a fluid is brought out of equilibrium by an applied temperature gradient the resulting effect is the occurrence of long-range correlations in the sound modes. This induced anisotropy can be probed by Brillouin light-scattering experiments.

The problem of Brillouin scattering in a fluid subjected to a temperature gradient $\vec{\nabla}T$ has been extensively discussed in a series of publications.[4–17] Although the basic assumptions of developed theories are different from each other, all of them arrive at a similar conclusion, an asymmetry being induced in the Brillouin lines when the fluid is exposed to a steady-state thermal flow. These lines are expressed by the structure factor

$$S^{\mathrm{ne}}_{\sigma B}(\vec{k},\omega)=\frac{[1-\sigma\epsilon_\sigma(\vec{k},\omega)]\Gamma_s k^2}{(\omega-\sigma v_s k)^2+(\Gamma_s k^2)^2}, \tag{1}$$

where σ is an index which can be $+1$ (anti-Stokes) or -1 (Stokes), corresponding to the emission or absorption of a sound wave propagating in the $\hat{k}$ ($\equiv\vec{k}/k$) direction. In the above expression $\vec{k}$ is the scattering wave vector, ω is the frequency, v_s is the sound velocity in the medium, and Γ_s is the classical sound attenuation coefficient. All of these parameters have to be computed at the center of the scattering volume, where the temperature is T. The extra term $\epsilon_\sigma(\vec{k},\omega)$ in the nonequilibrium structure factor indicates that the Brillouin lines are no longer symmetrical in the presence of a temperature gradient.

There is some controversy in the literature about the functions $\epsilon_+(\vec{k},\omega)$ and $\epsilon_-(\vec{k},\omega)$, but when the effect of finite size of the cell and nonlinearities in $\vec{\nabla}T$ are neglected, all theories give the same result for the integrated intensities of the Brillouin peaks:

$$I^{\mathrm{ne}}_{\sigma B}\equiv\int_{-\infty}^{+\infty}d\omega\; S^{\mathrm{ne}}_{\sigma B}(\vec{k},\omega)=\pi\left[1-\sigma\frac{v_s}{2\Gamma_s T}\,\frac{\hat{k}\cdot\vec{\nabla}T}{k^2}\right]. \tag{2}$$

If we define the quantity

$$\epsilon_B\equiv\frac{I^{\mathrm{ne}}_{-B}-I^{\mathrm{ne}}_{+B}}{I^{\mathrm{ne}}_{-B}+I^{\mathrm{ne}}_{+B}}, \tag{3}$$

as a measure of the "static" asymmetry, we will then have

$$\epsilon_B=\frac{v_s}{2\Gamma_s T}\,\frac{\hat{k}\cdot\vec{\nabla}T}{k^2}. \tag{4}$$

This effect is related to long-range correlations in the fluid due to the coupling of heat modes (nonprogressive phenomena) with sound modes. Choosing the scattering geometry such that $\vec{k}$ is parallel to $\vec{\nabla}T$ ($\hat{k}\cdot\vec{\nabla}T>0$), that is, antiparallel to the thermal flow, then there will be more sound waves with wave vector $-\vec{k}$ absorbed than sound waves with wave vector $+\vec{k}$ emitted.

A direct experimental check of the above results has been first provided by Beysens, Garrabos, and Zalczer, using water,[18] but for conditions where finite-size effects were clearly evident. The Brillouin asymmetry ϵ_B has been measured, but about three times weaker than predicted in Eq. (4). Kiefte, Clouter, and Penney[19] have repeated the experiment on water, under conditions more suitable for checking linear theories, but with a weak remaining boundary effect. Water has a small Brillouin scattering cross section compared to other liquids and it has the unavoidable presence of diluted dust, which scatters light strongly at the low scattering angles required by this kind of experiment.

So, it is important to obtain more experimental data using other liquids under suitable experimental conditions to confirm the validity of simple linear nonequilibrium theory. We report in this paper data obtained from benzene (C_6H_6) and isopropyl alcohol [$(CH_3)_2CHOH$] which have values of v_s and Γ_s comparable to those of water (see Table I), but with larger Brillouin scattering cross sections.[24–27] Beside this, these fluids are easily found in pure form with low chemical or dust contamination.

The problems attending a high curvature of the light path in a medium with large $\partial n/\partial z$, where n is the refractive

TABLE I. Some relevant parameters for the liquids of interest, with T = 320 K (center of the scattering volume) and λ = 514.5 nm.

Liquid [a]	n	$10^{-5}v_s$ (cm s^{-1})	$10^2\Gamma_s$ [c] (cm^2 s^{-1})	$10^4\left(\frac{\partial n}{\partial T}\right)_p$ (°C^{-1})
Water [b]	1.33	1.50	1.3	−0.8
Benzene	1.48	1.19	1.4	−6.5
Isopropyl alcohol	1.36	1.06	2.0	−5.2

[a] Most of the data were compiled from Refs. 20–22.

[b] For water see Ref. 23.

[c] To estimate Γ_s we have used the relation $4\pi^2\Gamma_s = v_{0s}^3(\alpha/\nu^2)_0$, where v_{0s} is the sound velocity at the low frequency limit and $(\alpha/\nu^2)_0$ is the frequency-independent absorption coefficient. The available data for this coefficient are taken from Ref. 20.

index and z is the direction of the temperature gradient, were overcome by careful choice of geometry.

Using data from Table I, for an applied temperature gradient of $|\vec{\nabla}T| = 50$ K cm^{-1} and a scattering angle of 25 mrad ($k = 4500$ cm^{-1} for benzene) we expect ϵ_B will have the theoretical value 3.3% for benzene and 2.4% for isopropyl alcohol, against 5.5% expected for water. However, the improved signal to noise ratio in the raw Brillouin spectra, due to the larger cross sections and much reduced scattering from particulate contaminants, more than compensates for the smaller expected asymmetries, leading to good overall data quality.

The experimental setup for measuring the Brillouin asymmetry is depicted in Fig. 1. The exciting light was provided by a Coherent Radiation CR-8 argon ion laser, oscillating cw in single longitudinal mode at the green line ($\lambda_0 = 514.5$ nm) with output power up to 250 mW. The incident light was spatially filtered (SF), then focused in the sample cell (SC) through an objective lens (O). Stray light and light in the laser frequency, coming from cell windows, were avoided putting a light trap (LT) after the cell. The scattered light was selected at the scattering angles of interest by means of a slit (S). The larger dimension of the slit was chosen in the direction orthogonal to $\vec{\nabla}T$, in order to minimize the influence of the uncertainty in the selected scattering vector $\vec{k}$ over the parameter of interest, $\hat{k}\cdot\vec{\nabla}T$. The scattered light was spatially filtered and collimated by a lens (L) and a 50-μm-diam pinhole (P), and then analyzed by a single-pass plane Fabry-Perot spectrometer tuned to 454.1 MHz free spectral range. The transmitted light was detected by a cooled RCA C31034 photomultiplier tube (PMT) in photon-counting mode. The accumulated count was read by a digital homemade data acquisition and stabilization system.

Stabilization of the Fabry-Perot spectrometer was achieved by a software routine and a hardware device that established continuous control over the transmission and finesse of the thermally isolated apparatus. This was made by monitoring the alignment of the reflective plates via inspection of the elastic (Rayleigh) peak. Tilt corrections as required were made in the intervals between sweeps by changing the voltages on the three Spectra-Physics 415A piezomicrometers (PZ in Fig. 1) mounted at 120° from each other, and holding one of the Fabry-Perot plates. Sweep motion was provided independently by a Burleigh RC-72 PZT Stack Assembly (SA), holding the other Fabry-Perot plate of the spectrometer.

The mean resolution of this system during a real experiment was 15 MHz, about two times the resolution expected from the reflectance of the plates. When we compare this resolution to the expected half width at half maximum (HWHM) of the Brillouin lines ($\Delta\nu_B = \Gamma_s k^2/2\pi \sim 0.05$ MHz), we see that is not possible to resolve the spectrum in the frequency domain. The whole apparatus can only furnish the integrated intensity of a Brillouin peak.

The scattering cell was made of two copper plates with epoxied stainless steel sides, which has low thermal conductivity coefficient. The entrance and exit windows were made of good planicity (λ/8 minimum) optical glass, AR coated for minimizing spurious elastic light from being dispersed at the windows. These windows were sealed with viton o-rings, which withstand chemical attack from the relevant organic liquids. We have used precise spacers during the cell assembly, so ensuring the dimension along $\vec{\nabla}T$ is $\Delta z = 1.00$ cm ($\pm 1\%$). The cell's interior volume was $4\times 5\times 1$ cm^3, and $\vec{\nabla}T$ was always maintained upward to avoid occurrence of fluid convection. The lower plate was cooled by circulating cold water on an attached aluminum block. The temperature of this plate was $T - \Delta T/2 \approx 294$ K and was monitored by a Tektronix Temperature Probe. The temperature $T + \Delta T/2$ of the upper plate was maintained constant by means of an electronically controlled heater, driven by a thermistor mounted at the plate. ΔT was kept constant within ± 0.1 K during and between runs.

As the liquids used have a low boiling point (~ 80 °C), a maximum $|\vec{\nabla}T| = \Delta T/\Delta z = 50$ K cm^{-1} was attained. Greater gradients generated vapor bubbles inside the liquid, risking a dangerous overexposure of the photomultiplier. The good

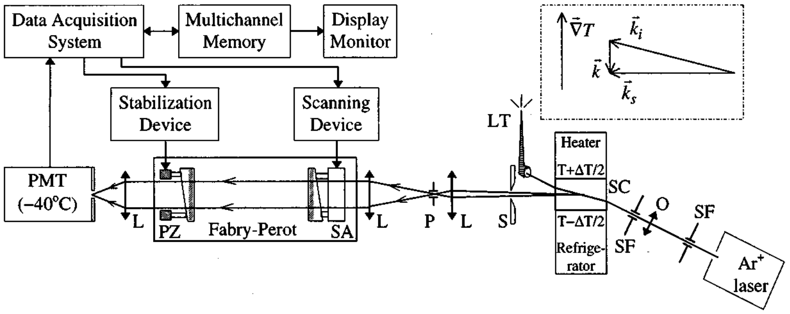

FIG. 1. Schematic diagram of experimental setup and scattering geometry (see inset); $\vec{k}_i$ is the wave vector of the exciting beam, $\vec{k}_s$ is the wave vector of the scattered light, and $\vec{k}$ is the scattering wave vector.

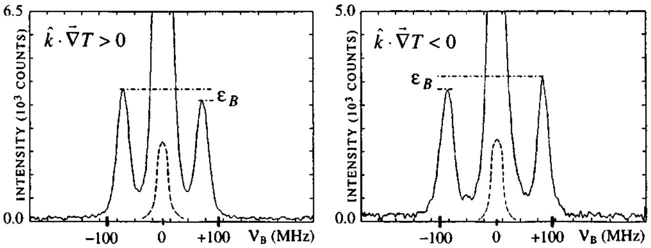

FIG. 2. Experimental spectra for benzene, examples at 4000 cm^{-1}, with $|\vec{\nabla}T|=43$ K cm^{-1} and $T=318$ K ($\hat{k}\cdot\vec{\nabla}T>0$), and at 4400 cm^{-1}, with $|\vec{\nabla}T|=40$ K cm^{-1} and $T=319$ K ($\hat{k}\cdot\vec{\nabla}T<0$), respectively. The inset shows the central peak (dotted line), reduced by the factor 5×10^{-2}.

quality liquid samples were subjected to an extensive fivefold filtering cycle through 0.1 μm teflon Millipore filters. The cell was washed about 70 times each cycle, and the final sample was allowed to rest on the cell for about 24 h before running the experiment.

The outside faces of the optical windows were cleaned with methanol between runs. Even so, the contribution of light scattered from the entrance and exit window surfaces was troublesome. We minimized it by imaging on the Fabry-Perot entrance pinhole (P in Fig. 1) just the center portion of our cell.

We have taken about 250 spectra, each one lasting for approximately 1/2 h of accumulation time (over 100 sweeps each spectrum); the ratio between the integrated intensities of the central (elastic) peak to the Brillouin peak was ~10. This indicates low dust contamination of the samples, as can be compared to more than 2 days of accumulation time and a ratio of ~2000 found in the experiment of water (see Ref. 18). These spectra have generated over 20 data points we describe here, each one of which having been obtained by a statistical mean of about 10–15 spectra taken at approximately the same experimental conditions (same $\vec{k}$, $\vec{\nabla}T$, etc.). Figure 2 shows typical spectra for benzene.

The resulting experimental asymmetry ϵ_B^{expt}, as a function of the reduced variable $k^{-2}\hat{k}\cdot\vec{\nabla}T$, is plotted in Figs. 3(a) and 3(b) for benzene, and in Fig. 3(c) for isopropyl alcohol. The value of k data used to compute the reduced variable was directly obtained from the measured Brillouin shifts ($\pm\omega_B=\pm v_s k$) in the spectra. This has an uncertainty of less than 1%, but the overall uncertainty in k is typically 5%, due to finite sizes of the focused beam in the scattering volume and of the scattering angle selection slit. The range of variation of k, of $|\vec{\nabla}T|$ and of the temperature T, at the center of scattering volume, was 4000−6300 cm^{-1}, 38−50 K cm^{-1}, and 316−324 K for benzene, while 3800−6100 cm^{-1}, 42−50 K cm^{-1}, and 318−323 K for isopropanol.

Typical uncertainty in ϵ_B^{expt} is estimated to be randomly distributed and less than 0.7×10^{-2}. From Figs. 3(a), 3(b), and 3(c) we see that the linear dependence of ϵ_B^{expt} with the reduced variable is clearly verified. The solid lines in these plots are least squares fittings, independently made for the two sides $\epsilon_B^{\text{expt}}>0$ and $\epsilon_B^{\text{expt}}<0$ in the case of benzene, while the dashed lines are the expected theoretical slopes $v_s/2\Gamma_s T$ [see Eq. (4)] as determined by the tabulated data on Γ_s. The measured experimental slopes are slightly greater than expected, ~26% for benzene and ~11% for isopropanol. The experimental values of the classical sound attenuation coefficient are $\Gamma_s^{\text{benz.}}=(1.1\pm0.2)\times10^{-2}$ cm^2 s^{-1} and $\Gamma_s^{\text{isopr.}}=(1.8\pm0.3)\times10^{-2}$ cm^2 s^{-1} (see Table I for comparison).

Our results have shown excellent agreement with linear theory, taking into account the uncertainty of about 20% in available Γ_s data. This was possible because we have carefully kept some experimental conditions close to the limits required by simple linear theory. As discussed in the literature,[5,11,12,15,17] all factors (i) $(kL)^{-1}$, (ii) l_s/L, (iii)

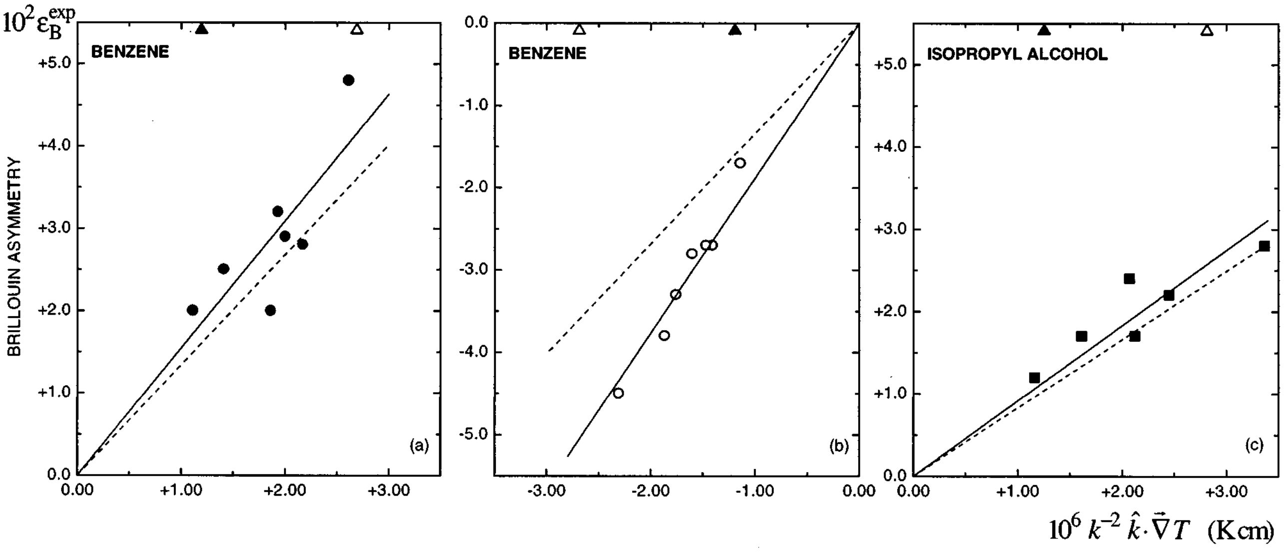

FIG. 3. Measured intensity asymmetry vs a reduced parameter for (a) benzene and (c) isopropyl alcohol, with $\hat{k}\cdot\vec{\nabla}T>0$. Data for benzene are again shown in (b), but with $\hat{k}\cdot\vec{\nabla}T<0$. Outer open triangles at the top indicate 4000 cm^{-1}, inner solid triangles 6000 cm^{-1}, for mean values of $|\vec{\nabla}T|_m=43$ K cm^{-1} for benzene, $|\vec{\nabla}T|_m=45$ K cm^{-1} for isopropyl alcohol.

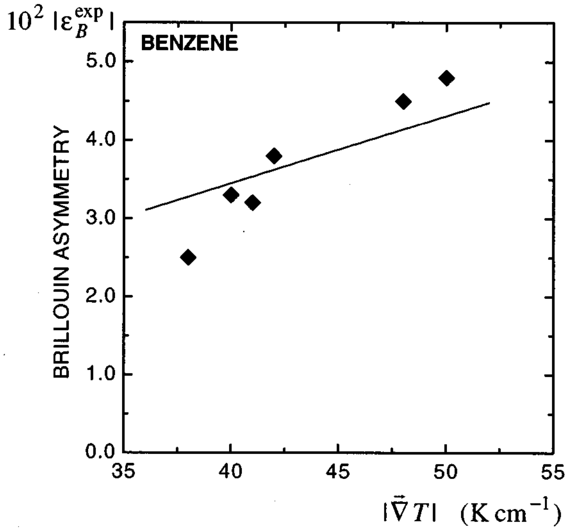

FIG. 4. Brillouin intensity asymmetry for benzene vs an applied temperature gradient with a fixed scattering vector (both signs), corresponding to a scattering angle of 25 mrad. The solid straight line is the best fit, taking into account that this line passes through the origin ($\epsilon_B^{\mathrm{expt}}=0$ when $|\vec{\nabla}T|=0$). The origin is not shown in the figure.

$l_s/\Delta z$, (iv) L/L_∇, and (v) l_s/L_∇ must be much less than unity for linear theory to apply. L is the size of the scattering volume, $l_s=v_s/\Gamma_s k^2$ is the mean free path for sound modes, and $L_\nabla \equiv T/|\vec{\nabla}T|$ is a typical length characteristic of the applied temperature gradient.

Conditions (i) and (ii) are also needed to observe Brillouin spectra in equilibrium situations: (i) guarantees there are many spatial periods of sound waves in the region under investigation and (ii), a condition more restrictive than the first, basically express that the uncertainty in the location of Brillouin lines associated with the finite size of the scattering volume is much less than the natural linewidth (HWHM). In our experiments the typical size of the scattering volume is determined by the lens used to focus the incident beam into the cell and by the vertical dimension of the selection slit, so $L\approx 0.2$ cm. By the stated range of measured k, we expect $(kL)^{-1}$ less than ~ 0.001 for both samples and $l_s/L \sim 1.0-2.0$ for benzene, while $l_s/L \sim 0.5-1.5$ for isopropyl alcohol. Thus, as the values of l_s/L indicate, it is not possible to resolve the experimental line shape.

The remaining conditions are related to applicability of linear theory. Condition (iii) is the key to neglect the boundary effects related to the finite size of scattering cell. It implies that a sound wave is essentially damped before being reflected at cell walls. For our data, $l_s/\Delta z$ ranges between 0.2 and 0.4 in benzene and 0.1 and 0.3 in isopropyl alcohol and we then expect no finite-size effects to be affecting the experiment. This is strengthened by the fact that wavelength of sound waves ranges between 10 and 15 μ m, one order of magnitude less than the estimated roughness of the copper plates, and one expects the efficiency of reflections on the walls to be very small. Finally, conditions (iv) and (v) allow for neglect of nonlinearities in the theory. Condition (iv) guarantees that the scattering occurs in a region where the temperature is essentially uniform, so we could in principle neglect the temperature dependence of the transport and thermodynamic parameters in the determination of the nonequilibrium steady state. The last condition indicates that the established sound waves are damped before they have time to probe regions with different temperatures. This implies the temperature gradients are not large, so one could neglect powers $\geqslant 2$ in the expansions over $|\vec{\nabla}T|$. In this work $L_\nabla > 6.4$ cm $(=320\ \mathrm{K}/50\ \mathrm{K\,cm^{-1}})$, so L/L_∇ is less than ~ 0.03 for both liquids and $l_s/L_\nabla \sim 0.031-0.062$ for benzene and $\sim 0.016-0.048$ for isopropanol.

We have also collected some spectra for benzene corresponding to a fixed scattering angle θ =25 mrad ($\pm 4\%$), thus to a fixed scattering vector $\vec{k}$. These data can be used to check the linear dependence of the induced asymmetry on $\vec{\nabla}T$, as shown in Fig. 4, where this is well verified.

Thus, we have checked that the predicted asymmetry induced in the Stokes and anti-Stokes lines of Brillouin spectra of fluids, other than water, brought out of equilibrium by a steady-state temperature gradient is experimentally verified. The liquids used as samples are characterized by a large $(\partial n/\partial T)_p$, which makes the experiment inherently difficult to perform. By restricting carefully the experimental conditions, we have also shown that the experimental data are in excellent agreement with simple linear theory within a factor very close to unity (~ 1.26 for benzene and ~ 1.11 for isopropyl alcohol), in spite of the complexity of both liquids and in view of the polar nature exhibited by one of the samples. The results, otherwise, indicate a general behavior of the effect in fluids that is not directly related to their molecular structure.

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