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Experimental Evidence for Brillouin Asymmetry Induced by a Temperature Gradient

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Very-low-angle Brillouin light-scattering experiments have been performed in liquid water subjected to a temperature gradient. The line intensities are unequal, and both the sign and the order of magnitude of this effect agree with recent theoretical calculations for nonequilibrium systems.

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Recently a number of theoretical predictions have been made concerning fluids out of equilibrium.[1-5] Although they start from different basic assumptions, all the theories give the same general result, i.e., when a fluid is brought out of equilibrium by a steady temperature gradient ∇T, long-range correlations should appear, leading chiefly to a modification of the structure factor $S(\vec{q},\omega)$ which would exhibit an extra $1/q^2$ term. This can be tested by a light-scattering experiment, more precisely in the Brillouin spectrum, whose lines are expected to show different intensities:

$$S(\vec{q},\omega)=[1\pm\epsilon(\vec{q},\omega)]\,\Gamma q^2/[(\omega\pm vq)^2+(\Gamma q^2)^2].$$

Here $\vec{q}$ is the transfer wave vector, v is the sound velocity, and ω is the angular frequency. Γq^2 corresponds to the sound damping and is the half-width at midheight of the Brillouin lines at equilibrium. $\epsilon(\vec{q},\omega)$ is in general a complex—and debated—function of $\vec{q}$ and ω. Here we will be concerned only with the *static* (integrated) intensities of the Brillouin lines, and in this case ϵ reduces to

$$\epsilon=\frac{v}{2\Gamma}\,\frac{\hat{q}\cdot\nabla T}{T}\,\frac{1}{q^2},$$

with $\hat{q}=\vec{q}/q$. This formulation corresponds, in fact, to the similar situation in crystals[6] where heat is carried only by phonons. To a temperature gradient corresponds a heat flux, and therefore an increase of the phonon density at a given $\vec{q}$ vector, varying as $1/q^2$. This increases the intensity of the Brillouin line which corresponds to fluctuations propagating in the direction of the heat flux (i.e., $-\nabla T$), and lowers the intensity of the other line.

It is of prime importance to verify this prediction experimentally. Indeed, if the statistical methods have been well verified to apply for systems at equilibrium, up to the present time no experimental verification has been given of the methods used in physics out of equilibrium.

The long-range contribution $1/q^2$ implies that experiments had to be performed at very low scattering angles. (See Fig. 1.) As a fluid, we used water near room temperature and atmospheric pressure, despite the fact that it is a poor light scatterer and that it is difficult to remove the dust, which scatters chiefly at small angles. However, the small variation of the refractive index with temperature allows high-temperature gradients to be applied without giving rise to spurious effects due to the beam bending and to defocusing (thermal lens). The experiments were carried out with the temperature kept near 40 °C.

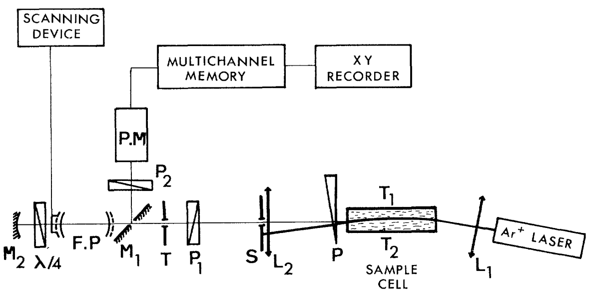

FIG. 1. Experimental setup: L_1 and L_2, lenses; P, prism; P_1 and P_2, polarizers; M_1 and M_2, mirrors; S, slit; T, pinhole.

At this temperature, $v=1.53\times10^5$ cm/sec and $\Gamma=1.30\times10^{-2}$ cm^2/sec.[7] The smallest scattering angle attainable was 0.7° ($q\simeq 2000$ cm^{-1}). The Brillouin shift is thus 3×10^8 rad/sec (50 MHz), the half width is 5.2×10^4 rad/sec (0.008 MHz), corresponding to a mean free path of fluctuations $l=v/\Gamma q^2\simeq 3$ cm. With a gradient $|\nabla T|\simeq 100$ K/cm, the expected asymmetry in the Brillouin intensity is about 50%.

The cell was composed of two copper plates (12 cm×5 cm) maintained at constant temperatures within 0.1 K by circulating water from thermostatic baths. The upper plate was at a temperature higher than that of the lower plate in order to prevent convection phenomena. The water was confined between the plates by means of a transparent Plexiglass frame. The spacing between the copper plates was $e=0.515$ cm, allowing temperature gradients of about 100 °C/cm to be obtained. The temperature difference was measured and controlled by thermocouple junctions placed inside the two copper plates. During an experiment (recording time: 1 or 2 days) the gradient was maintained constant within 1%. Deionized water was used. Between runs the water was filtered through 0.2-μm Teflon filters.

The scattering wave vector was selected by means of a slit whose larger dimension was always maintained perpendicular to $\vec{q}$. The uncertainty on $\vec{q}$ is typically 10%, due to the finite dimensions of both the slit and the beam. We used a 213.545-MHz free-spectral-range confocal Fabry-Pérot spectrometer which was piezoscanned and could be used either in a single-pass or a double-pass arrangement, the latter providing a much better contrast. The light source is a monomode argon-ion laser of 200 mW power whose beam (diameter, 0.02 cm) is slightly focused in the sample. The frequency drifts of both the laser and the Fabry-Pérot spectrometer are compensated by a triggering technique associated to a multichannel memory.[8] Because of the vibrations of the laser tube ("jitter"), the resolution corresponding to the half-width at midheight of the apparatus function (5.7 MHz) was about 4 times the resolution expected from the reflection factor (1.3 MHz), but this spurious effect had no influence on the contrast, which was found to be larger than 5×10^5 in the double-pass arrangement. When compared to the natural Brillouin linewidth (0.008 MHz), this resolution prevents any attempt being made to resolve the spectrum. In any case, some other limitations occur (see below), which prevent improvement of the resolution. Finally, the *sign* of the frequency shift with respect to the incident laser frequency was determined by using, in place of the sample, an electro-optic modulator working at 40 MHz.

In such a low-angle and strongly temperature-dependent experiment, we have to carefully consider the following points:

(i) The sound velocity variation in the observed volume, $\Delta v=(\partial v/\partial T)_p|\nabla T|\Delta Z$, where ΔZ is the full height difference of the illuminating beam in the same direction as ∇T. ΔZ is partly due to the beam diameter and partly due to the bending of the beam in the temperature gradient. Typically $\Delta Z\lesssim 0.1$ cm, and with $(\partial v/\partial T)_p\simeq 200$ cm sec^{-1} K^{-1},[7] $|\nabla T|\lesssim 100$ K cm^{-1}, the uncertainty is $\Delta v\lesssim 2\times10^3$ cm/sec, leading to an apparent linewidth broadening, $\Delta\omega=\vec{q}\cdot\Delta\vec{v}\simeq 4\times10^6$ rad/sec (0.6 MHz) at $q=2000$ cm^{-1}. This is negligible with respect to the Brillouin shift and the Fabry-Pérot spectrometer resolution, but it is 100 times the true linewidth.

(ii) The linewidth variation, $\Delta\Gamma=(\partial\Gamma/\partial T)_p|\nabla T|\times\Delta Z$. With the data of Ref. 7, $\Delta\Gamma/\Gamma\simeq 15\%$, which is negligible when the linewidth broadening from (i) is considered, and remains weak when the value of ϵ has to be estimated.

(iii) The influence of the finite aperture angle, of the finite beam diameter, and of the defocusing effects due to the gradient. Indeed, in water the second-order derivative of the refractive index $(\partial^2 n/\partial T^2)_p$ is not negligible at high temperature gradient, leading to a cylindrical-lens effect. Typically, the uncertainty Δq varies from 5% ($|\nabla T|=0$), to 10% ($|\nabla T|\simeq 100$ K/cm). At $q\simeq 2000$ cm^{-1}, the broadening varies from 1.5×10^7 rad/sec (2.5 MHz, $|\nabla T|=0$), to 3×10^7 rad/sec (5 MHz, $|\nabla T|\simeq 100$ K/cm). This effect is weak enough to not very much alter the detection of the Brillouin lines but it is sufficiently high to be measured

TABLE I. The measured Brillouin intensity asymmetries and half-widths at midheight of the Brillouin lines, with corresponding wave vectors and thermal gradients.

q [a] (cm^{-1})	$\|\nabla T\|$ (K/cm)	sign of $\vec{q}\cdot\nabla T$	$10^2\epsilon_{expt}$ [b]	$10^{-6}\Gamma_B$ [c] (rad/sec)
3360	59	+	+4.3[d]	4
3420	59	+	+7.5[d]	4
3130	59	+	+3[d]	8.2
2760	0	0	0[d]	3.5
3220	59	−	−3.5[d]	7.8
2110	59	+	+8.84	9.7
2380	59	−	−11.74	11.9
2080	0	0	0	3.5
2120	59	0[e]	0	6.6
3060	83	+	+6.25	17.3
2720	92	+	+7.38	24.5
2590	93	+	+3.93	24.8
2100	84	−	−7.92	16.6

[a] q is deduced from the measured Brillouin shift.
[b] $\epsilon_{expt} = [I(\omega<0) - I(\omega>0)]/[I(\omega<0)+I(\omega>0)]$, where I is the integrated Brillouin intensity. The accuracy of $10^2\epsilon_{expt}$ is about 1.
[c] Half-width at midheight of the Brillouin lines, obtained by subtracting the apparatus function half-width (35.8×10^6 rad/sec) from the experimental half-width.
[d] The Fabry-Pérot spectrometer was used in single-pass arrangement.
[e] $\vec{q}$ is perpendicular to ∇T.

(see Table I).

(iv) The mean free path l of the sound waves compared to the dimension e of the cell in the gradient direction: $l/e \simeq 6$ at $q \sim 2000$ cm^{-1}. It is not easy to estimate the influence of this on ϵ_{expt}. Moreover, l varies strongly with T: At the top of the cell, $l \sim 8.5$ cm, and at the bottom, $l \sim 1.5$ cm.[7] Nevertheless, we can state that a wave which "feels" the gradient in a direction cannot be efficiently reflected so as to feel the gradient in the opposite direction, which, in principle, could cancel the effect of the gradient. The sound wavelength is indeed small ($\simeq 30$ μm) compared to the surface roughness of the copper plates ($\simeq 100$ μm), and the efficiency of the reflection can be expected to be weak.

The various results are given in Figs. 2, 3, and Table I. The check of the asymmetry was performed by changing the sign of $\vec{q}\cdot\nabla T$ under nearly the same experimental conditions, and verifying that the asymmetry in the Brillouin intensities is reversed. The lines remained symmetrical in intensity whenever $\vec{q}\cdot\nabla T = 0$, that is for $\nabla T = 0$ or $\vec{q}\perp\nabla T$. The measurement of this asymmetry was performed by integrating the lines after having subtracted the base line. The accuracy of ϵ_{expt} is typically 10^{-2}. In order to check the variation of the experimental value of

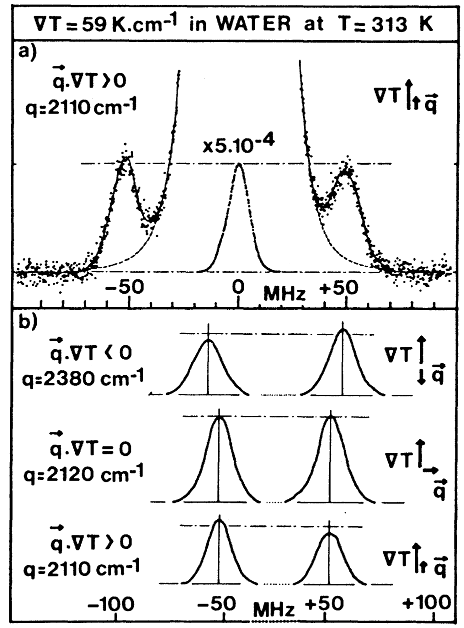

FIG. 2. (a) Experimental spectrum. The solid line is the best fit. The strong central peak (dotted line) corresponds to an elastic scattering by dust and windows. (b) Brillouin lines: Best fit for different orientations of $\vec{q}$ vs ∇T, showing that the intensities asymmetry varies as $\vec{q}\cdot\nabla T$.

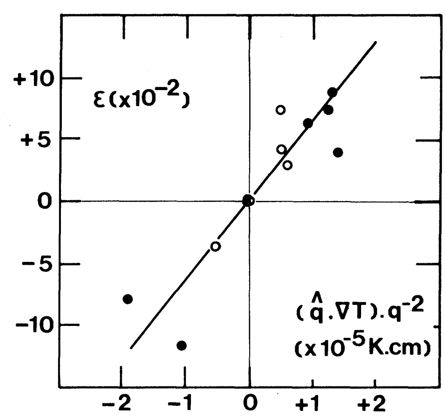

FIG. 3. Intensity asymmetry. $\epsilon_{expt} = [I(\omega<0) - I(\omega>0)]/[I(\omega<0)+I(\omega>0)]$ vs $\hat{q}\cdot\nabla T/q^2$. The expected variation is linear with slope $\simeq 19000$ cm^{-1} K^{-1}. The experimental slope is $\simeq 6700$ $cm^{-1} K^{-1}$ (straight line). Full points, with double-pass Fabry-Pérot spectrometer arrangement; open circles, with single-pass Fabry-Pérot spectrometer arrangement.

ϵ, $\epsilon_{\rm expt} = [I(\omega<0) - I(\omega>0)]/[I(\omega<0) + I(\omega>0)]$, with the reduced variable $\hat{q}\cdot\nabla T/q^2$, we determined the actual q vector by the experimental Brillouin shift $\omega_B = \vec{v}\cdot\vec{q}$. The accuracy was better than 0.5%. As shown in Fig. 3, the linear dependence of $\epsilon_{\rm expt}$ with $\vec{q}\cdot\nabla T/q^2$ is well verified, but the experimental slope $\epsilon_{\rm expt}[(\vec{q}\cdot\nabla T)/q^2]^{-1} \simeq 6700$ K^{-1} cm^{-1} is about 3 times weaker than the expected value $v/2\Gamma T \simeq 19\,000$ K^{-1} cm^{-1}. This may be due to the finite-size effect of the sample ($l/e \sim 6$).

We have experimentally shown that when a fluid is brought out of equilibrium by a temperature gradient, the structure factor determined by light scattering is changed by a long-range contribution, following $\hat{q}\cdot\nabla T/q^2$, which makes the Brillouin line intensities asymmetric. Both the sign and the order of magnitude of the effect have been found to be in agreement with the theoretical expectations, and thus provide a direct check of the statistical methods used in nonequilibrium physics. Spurious effects, due to the gradient itself, or to the geometry of the experiment, prevent any further investigation of the spectral shape being made. Finally, other systems, including solids, should exhibit an analogous behavior under a thermal gradient. This kind of experiment is in progress.

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Coherent-State Representation of Many-Fermion Quantum Mechanics

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An exact coherent-state representation is given for fermion systems which avoids the Gaussian overlap approximation in the reduction of the Hill-Wheeler-Griffin integral equation to a differential equation. An application shows that the random-phase-approximation ground-state correlation energy, derived with use of the Gaussian overlap approximation, is a factor of 2 too large.

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Slater determinants play a central role in many-fermion quantum mechanics primarily because we cannot solve the many-body problem and so resort to independent-particle approximations of one kind or another. As discussed recently elsewhere,[1,2] the set of Slater determinants constitutes a manifold that is well known in the mathematical literature as the Grassman manifold. It has many valuable properties being both Riemannian and symplectic. In particular, the latter means that it is a phase space. Furthermore, the quantum dynamics constrained to this manifold defines [time-dependent Hartree-Fock (TDHF)] equations of motion, which are just Hamilton's equations. For this reason the TDHF approximation may be regarded as a semiclassical approximation and it is of interest to discover how the quantal effects, suppressed by constraining the dynamics, can be restored by "requantization."

Attempts at the requantization have invariably followed the Hill-Wheeler-Griffin (HWG) method of generator coordinates.[3,4] Let $|\lambda\rangle$ denote a point on a line in the Hilbert space indexed by a parameter λ. The HWG method is to seek a state $\int \psi(\lambda)|\lambda\rangle d\lambda$, where $\psi(\lambda)$ satisfies the integral equation

$$\int \langle\lambda|\,(H-E)|\lambda'\rangle\psi(\lambda')d\lambda' = 0.$$

More generally, $|\lambda\rangle$ might be a point on a mani-

