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Light Scattering from Nonequilibrium Interfaces[1]

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The asymmetry of the two Brillouin peaks of light scattered from capillary waves on a water–nitrogen interface subject to a temperature gradient has been observed using a Fourier transform heterodyne technique. The local oscillator is frequency-shifted by a few kilohertz to separate the Stokes and anti-Stokes components. Although the sign and the order of magnitude of the effect agree with linear theory, the magnitude of the experimental asymmetry is about one-half of that predicted by linear fluctuating hydrodynamics.

KEY WORDS: capillary wave; heterodyne; nonequilibrium interface; surface light scattering; water.

1. INTRODUCTION

Microscopic fluctuations of macroscopic variables play an important role in many physical phenomena both in and out of equilibrium. For more than a century, equilibrium fluctuations in systems ranging from simple molecular fluids to complex biological solutions have been studied both theoretically and experimentally. In the past two decades there has been much interest in nonequilibrium steady-state fluctuations [1, 2]. For nonequilibrium bulk fluids, a number of theoretical predictions were confirmed experimentally using laser light scattering. In particular, asymmetries in the spectra of the scattered light were found to be in agreement with theory [3–5]. Recently, it has been predicted that a similar asymmetry occurs in the spectrum of the light scattered from capillary waves (ripplons) on a fluid interface in the presence of a temperature gradient [6]. This paper reports the first results of a surface light-scattering experiment designed to verify this prediction.

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2. THEORETICAL BACKGROUND

Thermal fluctuations on a fluid interface cause propagating capillary waves of a very low amplitude (~ 10 Å). These propagating waves give rise to a Brillouin doublet in the spectrum of light scattered from fluid interfaces [7, 8]. In equilibrium, the Stokes and anti-Stokes Brillouin peaks have the same intensity since the populations, n_S and n_a, of capillary waves traveling in opposite directions are equal. In nonequilibrium, however, n_S and n_a are no longer equal and the spectrum becomes asymmetric.

We first use simple arguments to derive an expression for the asymmetry ε of the Stokes and anti-Stokes peak intensities, I_S and I_a, defined as[3]

$$\varepsilon \equiv \frac{I_S - I_a}{I_S + I_a} \approx \frac{n_S - n_a}{n_S + n_a} \tag{1}$$

At a high temperature T, the population n of capillary waves with angular frequency ω_c is proportional to the temperature,

$$n = \frac{k_B T}{\hbar \omega_c} \tag{2}$$

with k_B and $\hbar$ the Boltzmann and Planck constants, respectively. The population difference $n_S - n_a$ can then be approximated by

$$n_S - n_a \approx \frac{k_B}{\hbar \omega_c} \Delta T^* \tag{3}$$

with ΔT^* the "effective" temperature difference for a capillary wave along its mean free path l_c. Thus, if we write $\Delta T^* = l_c \hat{q} \cdot \vec{\nabla} T$, with $\hat{q}$ a unit vector along the wavevector of the capillary wave, $\vec{q}$, the asymmetry ε becomes

$$\varepsilon \approx \frac{n_S - n_a}{2n} \approx \frac{l_c \hat{q} \cdot \vec{\nabla} T}{2T} \tag{4}$$

Substituting the characteristic length scale of the temperature gradient

$$L_\nabla \equiv [\hat{q} \cdot \vec{\nabla} \ln T]^{-1} \tag{5}$$

into Eq. (4), one obtains

$$\varepsilon \approx \tfrac{1}{2}(l_c / L_\nabla) \tag{6}$$

[3] The definition of the asymmetry in Ref. 6 is larger by a factor of two.

A more rigorous derivation of the asymmetry using fluctuating hydrodynamics was recently published by Grant and Desai [6]. First, the equation of motion for the instantaneous position ζ of a fluid interface is derived from the linearized hydrodynamic equations [9]. Spontaneous thermal fluctuations, which are the cause of the time-dependent behavior of ζ, are taken into account by adding stochastic driving forces to the equation of motion. Next, the nonequilibrium ensemble average of the interfacial fluctuations in ζ is obtained from the fluctuation–dissipation theorem. For a system of low viscosity, the power spectrum of these interfacial fluctuations yields an asymmetry [6]

$$\varepsilon = \tfrac{3}{2}(l_c/L_\nabla) \tag{7}$$

This result should be compared to the one derived from simple arguments in Eq. (6). Although they both depend on the ratio of the mean free path to the length scale of the temperature gradient, the results differ by a factor of 3.

From the dispersion relation of capillary waves on a liquid–vapor interface [11],

$$\omega = \sqrt{\sigma/\rho}\, q^{3/2} + 2i(\eta/\rho)q^2 \tag{8}$$

one obtains for the mean free path of a capillary wave

$$l_c = \frac{\sqrt{\sigma\rho}}{2\eta} q^{-3/2} \tag{9}$$

where σ, ρ, and η are the surface tension, density, and shear viscosity of the liquid, respectively. Substituting Eqs. (5) and (9) into Eq. (7) one obtains

$$\varepsilon = \frac{3}{4}\frac{\sqrt{\sigma\rho}}{\eta} q^{-3/2} \hat{q} \cdot \vec{\nabla} \ln T \tag{10}$$

Since the asymmetry depends on both $q^{-3/2}$ and $\nabla \ln T$, experiments must be carried out at small scattering angles ($\sim 0.25°$) and large temperature gradients. Stray forward scattered light and instabilities at high gradients therefore complicate the measurements.

3. EXPERIMENTAL

To resolve the two Brillouin peaks for small wavevectors, a recently developed Fourier transform heterodyne (FTH) apparatus, which has a high spectral resolution (0.15 Hz) and directional sensitivity, was used. For a complete description of the experimental technique, the reader is referred

to Ref. 11. Experiments were carried out on mercury, octane, and water. Mercury was initially chosen because of the large ratio $\sqrt{(\sigma\rho)}/\eta$. Unfortunately the high surface tension results in low-amplitude capillary waves and therefore insufficient signal-to-noise ratios to observe the asymmetry. Measurements on octane yielded spectra with an excellent signal-to-noise ratio in equilibrium. In the presence of a temperature gradient, however, the system becomes unstable. In the present work, therefore, we report only on water, which yields a reasonable signal-to-noise ratio and which remains stable because the temperature dependence of the molecular parameters (σ, ρ, and η) is relatively small.

A schematic diagram of the surface light scattering apparatus is shown in Fig. 1. A collimated, 4-mW multimode He–Ne laser beam is split into two with a beam splitter: 5% of the beam serves as local oscillator, while the remainder illuminates the liquid surface. The main beam, which is polarized perpendicular to the plane of incidence, makes an angle of about 80° with the normal to the surface. The beam width near the surface is 2 mm, yielding a surface spot of about 10 mm. To observe scattering from capillary waves with wavevectors in the range of 60–80 cm^{-1} (frequency range, 0.6–1 kHz), the scattering angle must be smaller than 10 mrad. A polarizer in front of the photomultiplier tube is used to reject stray light.

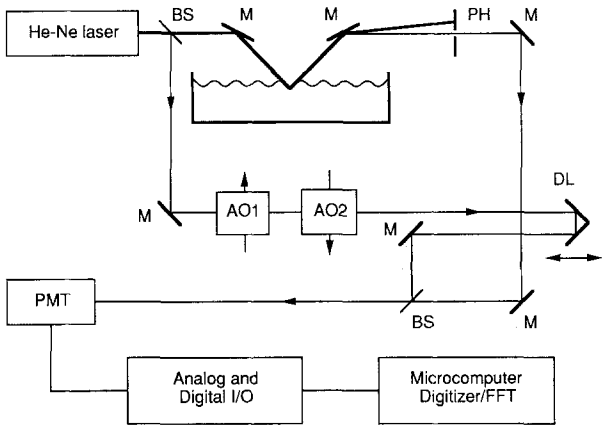

Fig. 1. Schematic diagram of the experimental setup. The surface of the liquid is probed with a multimode He–Ne laser beam. A local oscillator is derived from the same laser and frequency-shifted by a set of two acoustooptic modulators (AO1 and AO2). The beat signal of the scattered light with the local oscillator is recorded with a photomultiplier tube (PMT). M, mirror; BS, beam splitter; PH, pinhole; DL, delay line.

To separate the Stokes and anti-Stokes peaks the local oscillator is frequency-shifted by 3.5 kHz using two acoustooptic modulators [11].

The liquid is contained in a shallow black Delrin container ($0.075 \times 0.075 \times 0.004\ m^3$), located inside a sealed compartment ($0.66 \times 0.23 \times 0.23\ m^3$) made of black anodized aluminum. Much attention is paid to prevent dust and impurities from contaminating the interface. Distilled and deionized water is obtained from a Milli-Q system and prepared in a class 1000 clean room. Before each set of measurements the Delrin container is carefully cleaned and presoaked. Then the compartment is evacuated and flushed several times with filtered nitrogen gas to remove dust particles. Finally, the distilled and deionized water is introduced into the compartment and in the container by means of a feedthrough tube containing a 0.22-μm filter, and the compartment is filled with nitrogen gas at atmospheric pressure.

The temperature gradient along the surface is applied with a pair of copper plates that are temperature-controlled with two thermoelectric heat pumps (Fig. 2). The plates, which are spaced by 16 mm, are immersed about 1 mm below the surface to avoid distortion of the surface. Because of evaporation, the maximum workable temperature difference of the two plates is about 30 K. A liquid-cooled heat sink drains the excess heat from the heat pumps and prevents condensation of water vapor on the optics. The temperature of the plates is monitored by a pair of thermistors that

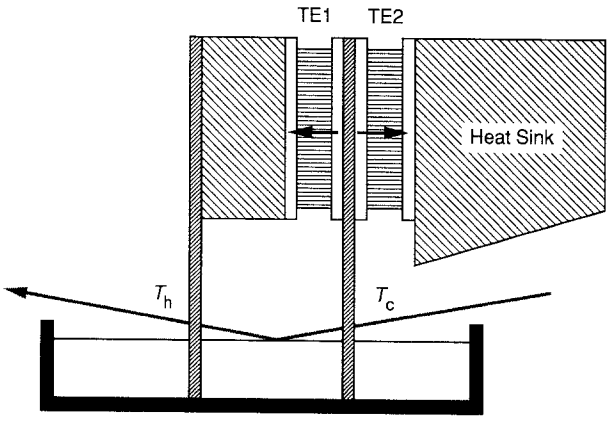

Fig. 2. Temperature-gradient assembly. A temperature gradient is applied along the surface by a pair of copper plates kept at temperatures T_h and T_c, respectively. The spacing between the plates is 16 mm. The temperatures of the plates are controlled with a pair of thermoelectric heat pumps (TE1 and TE2). Arrows indicate the direction of the heat flows. A water-cooled heat sink removes the excess heat from the heat pumps.

read the temperatures to within ± 0.1 K. The actual temperature profile along the surface was measured with a second pair of thermistors mounted on a translation stage. Because of convection, the profile is not linear, and the temperature gradient at the center between the two plates is about two times smaller than what one would expect for a linear profile.

In conventional surface light-scattering experiments carried out in equilibrium [12], separation of Stokes and anti-Stokes peaks is not necessary, and the local oscillator is produced by a diffraction grating. Alignment is then semiautomatic and insensitive to the motion of the interface. Because such a local oscillator is not frequency-shifted, however, this method is not appropriate for nonequilibrium measurements. To align the spectrometer in Fig. 1, a strong surface wave of the desired frequency is induced with a transducer. For high enough amplitudes, the Bragg scattered beam is visible and can easily be aligned with the local oscillator beam. Since the alignment is very sensitive to the motion of the interface, good vibration isolation of the system is necessary. Therefore the entire experimental setup is placed on an actively stabilized platform (Newport Corporation EVIS electronic vibration isolation system), which in turn is located on top of a pneumatically vibration-isolated optical table. The resulting stability of the surface is about 7×10^{-5} rad.

The beating signal between the scattered light and the local oscillator is recorded with a photomultiplier. The signal is sampled for 15 s at a 20-kHz rate by a GW Instruments MacAdios II computer interface, and the full signal trace is stored in the memory of an Apple Macintosh II com-

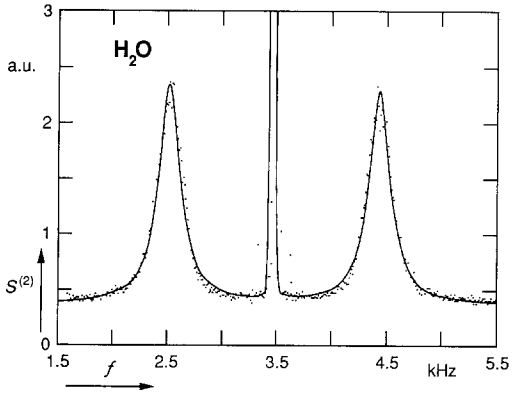

Fig. 3. Experimental spectrum showing the two Brillouin peaks around an intense central peak, which is due to stray elastic scattering of the incident laser light. The solid line is a least-squares fitted set of three Lorentzian lines to the data points.

puter. Next, the frequency spectrum of the digitized signal is obtained by a fast Hartley transform [13] (equivalent to fast Fourier transform but twice faster) of the stored signal. The resulting spectrum, an example of which is shown in Fig. 3, corresponds to the spectrum of the interfacial fluctuations [11]. To improve the signal-to-noise ratio, and because every now and then the measurements are disturbed by the formation of bubbles or by instabilities, this procedure was repeated eight times.

The relative intensities of the two Brillouin peaks are determined by fitting a set of Lorentzians to the averaged spectrum. Because the response of the digitizer is not completely linear, measurements without a temperature gradient show an asymmetry of about +2%. The asymmetry determined by the fitting procedure was therefore corrected for this equilibrium offset. It was verified that the corrected asymmetry can be reversed by reversing the sign of the acoustooptic frequency shift.

4. RESULTS AND DISCUSSION

The experimentally determined asymmetry for water at 286 K is shown as a function of $q^{-3/2}\nabla \ln T$ in Fig. 4. Each point is the average of eight measurements as explained in the previous section. The error bars represent the standard error of 0.4–0.6%. The sign of the effect was verified by observing the spectrum of light scattered from an induced wave traveling from the hot to the cold plate which shows only one side peak. In

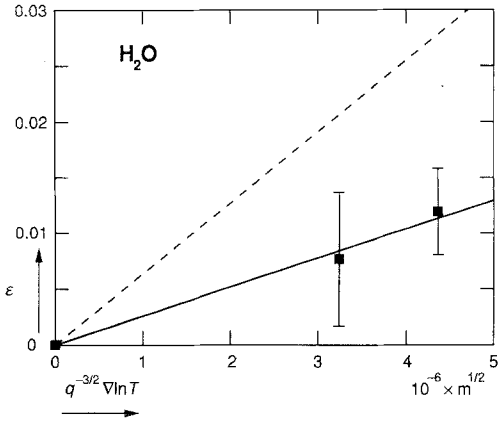

Fig. 4. Brillouin intensity asymmetry ε [as defined in Eq. (1)] versus $q^{-3/2}\nabla \ln T$. The expected slope according to Eq. (10) (dashed line) is $5.4 \times 10^3\ m^{-1/2}$. The experimental slope (solid line) is $(2.6 \pm 0.6) \times 10^3\ m^{-1/2}$.

addition, it was verified that the sign can be reversed by switching the direction of the acoustooptic frequency shift.

Figure 4 also shows the asymmetry predicted by Eq. (10), using literature values [14] for the density, surface tension, and viscosity at the temperature of the probing region. On the basis of this expression, one would expect a 2–3% asymmetry for a temperature gradient of $600\ \mathrm{K \cdot m^{-1}}$ and a capillary wavevector of $60\text{–}80\ \mathrm{cm^{-1}}$. With a standard error or less than 0.6%, such an asymmetry can easily be detected. As can be seen from the graph, however, the experimental slope is about one-half of that predicted by linear theory.

In light-scattering experiments on nonequilibrium bulk liquids [3], similar discrepancies have been observed and explained in terms of finite-size [15] and nonlinearity [16] effects. In a more recent experiment by Kiefte et al. [4], agreement with theory was obtained, and it was shown that finite-size and nonlinearity effects can indeed cause discrepancies. Qualitatively, finite-size effects play a role when the ratio of the mean free path l_c to the spacing L between the two plates is large or when the reflectivity R of the container walls is large. Nonlinear effects of the temperature gradient depend on the ratio of the mean free path to the characteristic length scale of the gradient, L_∇. Also, the ratio $\Delta T/T$ must be small enough to neglect the temperature dependence of the molecular parameters and to maintain a steady state. In the present setup, $l_c/L \leqslant 0.5$, $l_c/L_\nabla \leqslant 0.02$, and $\Delta T/T \approx 0.04$; this is comparable to the situation in the experiment by Kiefte et al. on bulk water, which is in good agreement with theory. Moreover, the spectrum for an induced capillary wave traveling in one direction has only one side peak, showing that $R \approx 0$ for our setup. Owing to the two-dimensional nature of our system, however, finite-size and nonlinearity effects may be more pronounced.

5. CONCLUSION

We have observed the asymmetry in the Brillouin spectrum of light scattered from a fluid interface subject to a temperature gradient. The sign and the order of magnitude of the effect agree with linear theory. Although the experimental condition is similar to that for the bulk experiments that show a good agreement with theory, the experimentally determined asymmetry is smaller than predicted by about a factor of two.

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