SPECTRAL ASYMMETRY IN THE LIGHT SCATTERED
FROM A NONEQUILIBRIUM LIQUID INTERFACE

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An asymmetry of the two capillary wave peaks in the light scattered from a water surface subject to a temperature gradient parallel to the surface has been observed using a Fourier transform heterodyne technique. The sign and order of magnitude of the effect agree with linear fluctuating hydrodynamic theory.

Currently there is much interest in understanding systems out of equilibrium. In particular, for steady states near equilibrium, extensive theoretical work has been done in the last two decades (see, e.g., reviews in ref. [1]). For nonequilibrium bulk fluids a number of theoretical predictions were tested experimentally using laser light scattering. For instance, the asymmetry in the spectra of light scattered from bulk liquids subject to a temperature gradient was compared with theory [2–4]. On the other hand, little work has been done on interfaces out of equilibrium, in spite of the large interest in interfacial phenomena. The main difficulty is the lack of translational symmetry across the interface. Recently, it was predicted, however, that in the presence of a temperature gradient the spectrum of the light scattered from a fluid interface also becomes asymmetric [5]. This Letter reports the results of a surface light scattering experiment that verifies this prediction.

Thermal fluctuations of molecules near an interface cause propagating capillary waves of very small amplitude. These waves give rise to a capillary-wave doublet in the light scattering spectrum from the interface [6,7]. In equilibrium, the Stokes and anti-Stokes peaks have the same intensity since the populations, n_S and n_a, of capillary waves travelling in opposite directions are equal. In nonequilibrium, however, n_S and n_a are no longer equal and the spec-

trum becomes asymmetric. The asymmetry ϵ of the spectrum can be defined as [1]

$$\epsilon(q) \equiv \frac{I_S - I_a}{I_S + I_a} , \qquad (1)$$

where I_S and I_a are the integrated intensities of Stokes and anti-Stokes peaks for a capillary wave of wavevector q. Since the integrated intensity is proportional to the peak intensity for a given linewidth, eq. (1) can be rewritten in terms of the power spectrum of the interfacial fluctuations [8], $S(q, \omega)$, as

$$\epsilon(q) \equiv \frac{S(q, -\omega_c) - S(q, \omega_c)}{S(q, -\omega_c) + S(q, \omega_c)} , \qquad (2)$$

with ω_c the angular frequency of the capillary wave. For a liquid–vapor system ω_c can be approximated by [9]

$$\omega_c(q) = \sqrt{\frac{\sigma}{\rho}} q^{3/2} + i\beta(q) , \qquad (3)$$

with q the magnitude of the wavevector q, and $\beta(q)$ the damping coefficient given by

$$\beta(q) = 2\frac{\eta}{\rho} q^2 , \qquad (4)$$

where σ, ρ, and η are the surface tension, density, and shear viscosity of the liquid, respectively. Using li-

[1] The definition of the asymmetry in ref. [5] is larger by a factor two.

nearized fluctuating hydrodynamic theory, an expression for the asymmetry in terms of molecular parameters was derived by Grant and Desai [5]. If $\beta \ll \omega_c$, and if the temperature gradient ∇T is not too large, the power spectrum of these interfacial fluctuations yields an asymmetry

$$\epsilon(q) = \frac{3}{4}\frac{\sqrt{\sigma\rho}}{\eta} q^{-3/2}\,\hat{q}\cdot\nabla\ln T\,,\qquad (5)$$

where $\hat{q}$ is a unit vector in the direction of the wave-vector q. Since the asymmetry is proportional to $q^{-3/2}$, experiments must be carried out at small scattering angle with a corresponding typical frequency, $f_c=\omega_c/2\pi$, on the order of a few kHz. A high resolution technique, such as optical heterodyne detection [10], is therefore required to spectrally resolve the power spectrum $S(q, \omega)$ of the interfacial fluctuations.

For optical heterodyning, the scattered laser light is mixed with a local oscillator derived from the same laser source. Beating then occurs at the difference frequency of the two beams. As long as the path difference of the two beams is within the coherence length of the light source, the frequency fluctuations of the laser itself cancel out. Thus, the power spectrum of the beating depends only on $S(q, \omega)$ and not on the spectrum of the laser.

In conventional surface light scattering experiments carried out in equilibrium [2,3,11], separation of Stokes and anti-Stokes peaks is unnecessary, and the local oscillator has the same frequency as the incident light. Since the beat frequency is insensitive to the sign of the frequency difference, the two Brillouin peaks then coincide in the beat spectrum. To measure the nonequilibrium asymmetry of the spectrum, however, it is essential to separate the two peaks. This can be accomplished by coherently shifting the frequency of the local oscillator by a small amount [12]. The optical frequency shift depends on the experimental configuration and the spectral range of the detection technique.

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
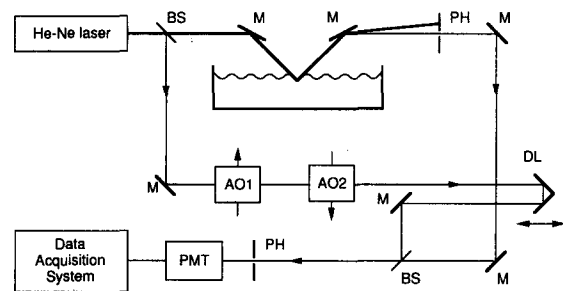

Fig. 1. Schematic diagram of the experimental setup. The surface of the water is probed with a multimode He–Ne laser beam. A local oscillator is derived from the same laser, and frequency-shifted by a set of two acousto-optic modulators (AO1 and AO2). The beam signal of the scattered light with the local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

about 75° with the normal to the surface. The beam width near the surface is 2 mm, yielding a surface spot of about 8 mm. For the observation of capillary waves with wavevectors in the 60–90 cm^{-1} range ($f_c=0.6$–1.2 kHz), the scattering angle must be smaller than 10 mrad. To separate the two Brillouin peaks in this frequency range, the local oscillator is frequency-shifted by 4.5 kHz using two 40 MHz acousto-optic modulators with a difference in carrier frequency of 0.0045 MHz [12].

The spectrometer in fig. 1 can easily be aligned when a strong surface wave of the desired frequency is induced with a transducer. For high enough amplitude, the Bragg scattered beam is visible and can 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. 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. For a water depth of 1 mm, the resulting stability of the water surface is about 7×10^{-5} rad.

The water is contained in a shallow black Delrin container ($75\times75\times4$ mm^3), located inside a sealed compartment ($0.66\times0.23\times0.23$ 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 100

clean room. Before each set of measurements the Delrin container is carefully cleaned and pre-soaked. The compartment is evacuated and flushed several times with filtered nitrogen gas to remove dust particles and then filled with nitrogen gas at atmospheric pressure.

The temperature gradient along the surface is applied by a pair of copper plates that are temperature-controlled with two thermoelectric heat pumps. The plates, which are spaced by 16 mm, are immersed about 0.1 mm below the surface to avoid distortion of the surface. To damp out long-wavelength gravity waves and to reduce convection the depth of the water sample is kept around 1 mm. 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 read the temperatures to within ±0.1 K. To determine the temperature gradient at the illuminated surface spot, the actual temperature profile along the surface was measured with a second pair of thermistors mounted on a translation stage.

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 using a microcomputer, and the frequency spectrum $S(q, \omega)$ is obtained by a fast Hartley transform of the sampled data points [13]. This procedure is repeated eight times to improve the signal-to-noise ratio. An example of the resulting averaged spectrum is shown in fig. 2.

Asymmetry values are determined by fitting a theoretical spectral shape to the experimental data points. The spectral shape can be obtained from linear response theory [14]. For a system of low viscosity it may be approximated by squared Lorentzians [5],

$$S(q, \omega) = \frac{8k_B T\eta q^3/\rho^2}{[\omega^2 - \omega_c(q)^2]^2 + 4\beta^2(q)\omega^2}, \quad (6)$$

or by Lorentzians [14]. Because of the divergence of the laser beam, the finite size of the pinholes, and residual motion of the surface, the experimental spectra are always convolved with some instrumental function. The best way to fit the data points therefore would be to use a convolution of the full expression from linear response theory, with the in-
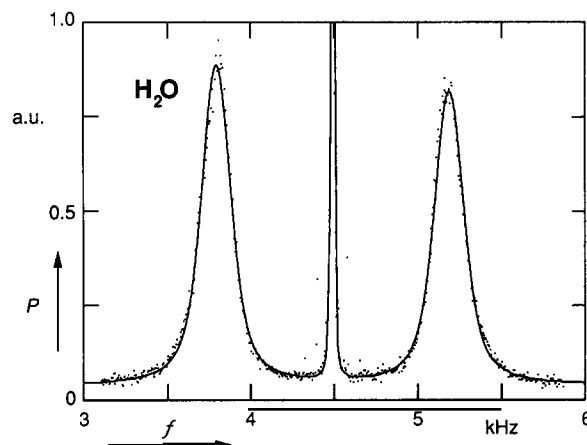

Fig. 2. Experimental spectrum for $q=92$ cm^{-1} and $\nabla T=9.5$ K cm^{-1} at $T=295$ K showing the two Brillouin peaks around an intense central peak, which is due to stray elastic scattering of the incident laser light. The solid line is a least-squares fitted set of two Voight profiles for the two side peaks and a Lorentzian for the central peak to the data points. The corrected experimental asymmetry as defined in eq. (1), ϵ_{exp}, is 0.006 while from eq. (5) $\epsilon_{th}=0.023$.

strumental function measured for a system with very small viscosity [15]. In general, however, the instrumental function is approximately Gaussian, and the measured spectrum can be approximated by a convolution of a Lorentzian and a Gaussian (Voigt profile) [16,17]. The asymmetries reported here were obtained from the nonlinear least-squares fitting with Voigt profiles which produced the best fit.

In fig. 3, the experimentally determined asymmetry, ϵ_{exp}, is compared with the theoretically predicted one, ϵ_{th}, from eq. (5), using literature values [18] for the density, surface tension and viscosity at the temperature of the probing region. Since the frequency response of the apparatus is not completely flat, the spectra taken in the absence of temperature gradient show a small instrumental asymmetry, ϵ_{inst}. All data were corrected for this small instrumental asymmetry. The error bar for the point at $\epsilon_{th}=0$ represents the standard deviation in ϵ_{inst} when $\nabla T=0$. The sign of the asymmetry can be reversed by reversing q. As shown in fig. 3, this indeed results in a sign change of the measured asymmetry. The slope of the experimental data points, represented by the solid line in fig. 3, is about three times smaller than expected on the basis of eq. (5). A number of pos-
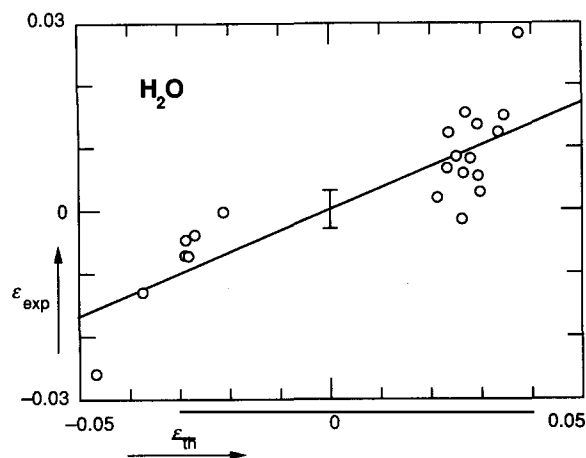
Fig. 3. Experimental Brillouin intensity asymmetry ϵ_{exp} versus theoretical asymmetry ϵ_{th} as given in eq. (5). The expected slope is 1. The experimental slope (solid line) is 0.35.

sible causes for the discrepancy are: (1) finite-size effect, (2) nonlinearity effects, (3) contamination of the surface, and (4) the fitting procedure. Each of these possibles causes is discussed below.

It is interesting to note, first, that in light scattering experiments on nonequilibrium bulk liquids [2], a similar discrepancy between measured and predicted asymmetry was found. In this case the discrepancy was attributed to finite size and nonlinearity effects [19,20]. In a later experiment by Kiefte et al. [3], agreement with the theory was obtained for a particular "best" data set, and it was shown that finite size effects, and, to a lesser extent, nonlinearity effects indeed affect the measurements. So far theoretical analyses of finite size and nonlinearity effects have only been carried out for bulk liquids.

In the case of a nonequilibrium interface, one expects finite size effects to play a role when the ratio of the mean free path [5],

$$l_c = \frac{\sqrt{\sigma\rho}}{2\eta} q^{-3/2},$$ (7)

to the spacing L between the two plates is large, or when the acoustic reflectivity of the container walls is large. In the present setup, using literature values for σ and η, $0.3 \leqslant l_c/L \leqslant 0.6$. Additional tests showed that the spectrum for an induced capillary wave travelling in one direction has only one side peak, in-

dicating that the acoustic reflectivity is negligible in our setup.

Nonlinear effects of the temperature gradient depend on the ratio of the mean free path to the characteristic length scale of the gradient,

$$L_V \equiv (\hat{q} \cdot \nabla \ln T)^{-1}.$$ (8)

In addition, 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, $l_c/L_V \leqslant 0.01$, $\Delta T/T \approx 0.1$; this is comparable to the situation for the best data set from the experiment by Kiefte et al. on bulk water, which is in agreement with theory. We attempted to investigate the dependence of the asymmetry on the temperature difference and the plate spacings. Unfortunately the relevant parameters could not be changed sufficiently to make any conclusive statements.

Contamination of the liquid surface could also partly account for the observed discrepancy. Contamination at the interface tends to lower the surface tension of the liquid, which in turn reduces the asymmetry (see eq. (5)). A Langmuir trough equipped with surface-cleaning mechanisms and a surface-tension monitor is being constructed for future experiments.

Finally, despite the excellent separation of the side peaks from the central one, the experimentally determined asymmetry depends somewhat on the background intensity at the position of the side peaks and on the lineshape used in the fitting procedure. While resulting in ref. [2] a poorer overall fit, fitting with simple or squared Lorentzians, for example, consistently produced about 30% larger values for the asymmetry. This, however, is too small a difference to explain the observed discrepancy of a factor of three.

In conclusion, the Fourier transform heterodyne (FTH) spectroscopy technique, with its directional sensitivity and high resolution, allows one to observe the broken translational symmetry on a nonequilibrium liquid interface. We have measured the asymmetry of the two Brillouin peaks of light scattered from a liquid–vapor interface subject to a temperature gradient. Our result agrees, in sign and order of magnitude, with the asymmetry predicted by linearized fluctuating hydrodynamics.

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