J. Phys. Chem. **1993,** *97,* 12876–12878

Direct Measurement of the Spatial Damping of Capillary Waves at Liquid–Vapor Interfaces

Ka Yee Lee,[†] Tom Chou, Doo Soo Chung,[‡] and Eric Mazur[*]

Department of Physics and Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

Received: June 28, 1993; In Final Form: August 31, 1993[⊗]

We measured the spatial damping of low-frequency surface waves at air–water interfaces using a novel heterodyne light-scattering technique. For pure water the measured damping agrees well with linear hydrodynamic theory. For interfaces covered with a monolayer of pentadecanoic acid, we find a 5-fold increase in damping at a surface concentration of 2.2 molecules nm^{-2}, near the high-density end of the gas/liquid-expanded coexistence region. The behavior of the damping as a function of surface concentration cannot be explained by existing theories.

The study of interfaces has attracted the attention of scientists throughout history. It has been known for a long time, for example, that a single surfactant monolayer at a liquid–vapor interface can lead to a dramatic attenuation of wave motion.[1,2] Recently, because of the many technological applications of surfactants and because of the biological importance of monolayer films, the properties of these quasi-two-dimensional systems have been the subject of renewed interest. In spite of much research, however, there still is a lack of experimental data on surface viscoelastic properties. Yet the damping of surface waves has been attributed to these viscoelastic constants.[3] Measurements of surface wave damping can therefore furnish information on surface viscoelastic properties.

A number of groups have used inelastic light scattering to study the damping of thermally excited capillary waves[4,5] caused by spontaneous fluctuations. In principle, the temporal damping coefficient can be obtained from the width of the inelastic peaks in the spectrum of the scattered light.[6] In practice, however, these peaks are instrumentally broadened. There is no direct method to determine the instrumental broadening, which frequently dominates the width, especially in the low-frequency regime. Other groups have studied capillary wave damping by looking at the deflection of a laser beam[7] by induced surface waves.[8] This technique works only for low-frequency surface waves, when the laser spot size is smaller than the surface wavelength. The results presented here were obtained using a novel differential light-scattering technique that is free of the difficulties mentioned above. We present data on capillay wave damping for pure water and pentadecanoic acid (PDA).

Interfacial waves of small amplitude caused a normal displacement of the interface, $\zeta = \zeta_0 \exp[i(kx - \omega t)]$, with ζ_0 the amplitude of the wave, k the wavevector, ω the frequency, and x the direction of propagation along the surface. From the linearized Navier–Stokes equation one obtains the following dispersion relation for waves on a liquid–vapor interface:[9]

$$[\sigma k^3 + \rho g k + i\eta\omega_0 k(k + m)\rho\omega_0^2][\epsilon k^2 + i\eta\omega_0(k + m)] + \omega_0^2\eta^2 k(k - m)^2 = 0 \quad (1)$$

with

$$m = k\sqrt{1 + i\omega_0\rho/\eta k^2}$$

and where η is the dynamic viscosity, ρ the density of the liquid, g the gravitational acceleration, and σ the equilibrium surface tension. In the absence of surface viscosity, ϵ is the complex surface dilation modulus.

For a pure interface ($\epsilon = 0$) in the low-viscosity limit, the frequency of a wave with real wavevector k, $\omega = \omega_0 - i\beta$, has a small imaginary component, $\beta = 2k_0^2\eta/\rho$, leading to temporal damping of the wave. This coefficient β can be obtained from the widths of the inelastic peaks in the spectrum of the light scattered from thermal capillary waves but requires deconvolution of instrumental line broadening.[4,5] Alternatively, the wavevector for a wave of fixed real frequency ω_0, has a small imaginary part contributing to spatial damping. Substituting $k = k_0 + i\alpha$ ($\alpha \ll k_0$) into eq 1 with $\epsilon = 0$, keeping only first-order terms in ν and α and neglecting the gravity term, we obtain

$$\alpha = 4\eta\omega_0/3\sigma \quad (2)$$

The spatial damping coefficient α is therefore related to β by $\beta = \alpha\ \partial\omega/\partial k$. In the experiment described below the spatial damping coefficient α is determined by measuring the exponential decay $e^{-\alpha x}$ of the amplitude of an induced surface wave.

In our experiment capillary waves of frequency $f_0 \equiv \omega_0/(2\pi)$ in the 0.5–2 kHz range are generated by applying a sinusoidal voltage ($\sim$ 100 V) of frequency $f_0/2$ to a metal blade placed about 1 mm from the interface.[7] For pure water, where eq 1 reduces to $\omega^2 = (\sigma/\rho)k^3 + gk$, these frequencies yield wavelengths of 0.5–1.2 mm. To probe the wave amplitude as a function of distance x, we use a heterodyne light-scatering technique described previously.[10] Since translating the probe spot is not practical, one must translate the blade to vary x. To compensate for any variation in the distance between the blade tip and the surface during translation, we use a differential technique and measure the ratio between wave amplitudes on both sides of the blade.

A schematic diagram of the experimental setup is shown in Figure 1. A 10-mW He–Ne laser beam is split into a main beam (M) and a much weaker (5%) local oscillator (LO). The frequency of the two beams is shifted using a pair of acoustooptic modulators, giving the beams a frequency difference $\Delta f = 5.1$ kHz.[10] The M and LO beams are focused onto a single 2-mm-diameter spot on the surface at an incidence angle of about 60°. The angle between the two beams is adjusted so as to make the difference of the incident light wavevectors match the induced surface wavevector.

An identical pair of M and LO beams is focused onto a second probe spot on the other side of the blade at a fixed distance d = 40 mm from the first. Since the induced waves travel in opposite directions at the two probe spots, the detected signals are at frequencies $\Delta f - f_0$ and $\Delta f + f_0$, respectively (see Figure 1). The two scattered light beams are combined and detected with a single photomultiplier tube. The photomultiplier signal is digitized at a 20-kHz rate and then Fourier-transformed to obtain the power spectrum of the scattered light.[10]

A typical spectrum is shown in Figure 2. It consists of an intense central peak at the carrier frequency Δf, and satellite peaks centered at $\Delta f \pm f_0$. The two sharp peaks result from the

---

[†] Current address: Department of Chemistry, Stanford University, Stanford, CA 94305-5080.

[‡] Current address: Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139.

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1993.

0022-3654/93/2097-12876$04.00/0