DETECTION OF THE RELAXATION OF THE STRETCHING MODE IN THIN LIQUID FILMS

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The stretching mode in thin (50 nm), free, liquid films has been examined by means of laser intensity fluctuation spectroscopy (heterodyne configuration). The power density spectra of the scattered intensity fluctuations show maxima in the MHz region, indicating the propagating character of the mode. The peak frequencies are related to the surface tension of the film.

We report measurements of the spectrum of light scattered from a thin, free, liquid film (soap film).

Our vertical free films consist of a thin liquid sheet bounded by liquid—air interfaces. The stability of the aqueous film is achieved by the presence of surface active HDTAB (hexadecyltrimethyl ammonium bromide) molecules. The ionic parts of these molecules, located in the interfaces, give rise to repulsion between the interfaces. If this repulsion is counter balanced by the London—van der Waals attraction between all molecules and the hydrostatic pressure, the film is in equilibrium (constant thickness h).

Due to the thermal motion of the molecules the film undergoes local thickness fluctuations and roughening giving rise to the scattering of light. The time behaviour of the thickness fluctuations is expected to be influenced by the interaction forces and the mechanical properties of the film system (e.g. surface tension and viscosity). Knowledge of these physical quantities is of great importance for understanding the stability of a number of colloidal systems (emulsions, foams) and also for a better understanding of biological membranes.

Light scattered from thermally excited surface waves on soap films, without considering the spectral distribution, was first considered by Vrij [1] and was recently thoroughly studied experimentally by Donners et al. [2]. The dynamics of the fluctuations can be studied by measuring the power spectrum (or correlation function) of the scattered intensity by means of laser intensity fluctuation spectroscopy.

The theory of the dynamics of the surface of the films can be considered along the following route. The surface corrugations are decomposed into Fourier components. Since there are two interfaces it is clear, from general considerations, that for each Fourier component, the film motion exhibits two modes: one in which the surfaces move antiparallel with respect to the normal (squeezing mode), one in which they move parallel (stretching mode, constant film thickness). For each mode, hydrodynamic theories have been developed to describe the liquid motion [3—6]. If the corresponding surface waves have the form $\exp(ikx - i\omega t)$, where k is the wave number of the Fourier component, x a space coordinate, ω the angular frequency and t is time, a dispersion relation $\omega(k) = 0$ is found from the linearized hydrodynamic theories. In fact, the real part of ω describes the propagation of the mode and the imaginary part its growth or damping. The general dispersion relation for the stretching mode is rather complicated but in the so-called long wavelength limit i.e. the wavelength Λ is large compared to the thickness h[‡] and with non-moving surfaces one has [4]

$$\omega^2 + ik^2 v - \omega_{02}^2 = 0, \tag{1}$$

[‡] This condition is always fulfilled in our experiments because the thickness of the film is in the nm region whereas the wavelengths are in the μm region.

where $v = \eta/\rho$ is the kinematic viscosity, ρ the mass density, $\omega_{02}^2 = 2\gamma k^2/\rho h$, $k = 2\pi/\Lambda$ and γ the surface tension of the film.

The roots of (1), appropriate to our problem; are complex conjugates so we expect a Brillouin doublet in the spectrum of the scattered light. The frequency shift is approximately[‡] given by the oscillating frequency $\omega_{02}/2\pi$ whereas the linewidth is given by the viscosity term $k^2 v$. Using bulk values for γ (= 35 mN/m) and v (= 10^{-6} m^2/s) one expects shifts in the MHz region and (full) linewidths in the kHz region for our relevant k and h values.

In this letter we report on the stretching mode. Dynamic light scattering experiments on the squeezing mode have been reported elsewhere [4,7,8], but as far as we know such experiments have not been published on the stretching mode.

The experimental set-up is as follows: Light from an argon laser, operating in the 514.5 nm or 488 nm TEM$_{00}$ mode at a power of $\approx$ 500 mW, inpinges on the film. The angle of incidence is 60° and the light is polarized perpendicular to the plane of incidence. Conservation of the component of momentum along the liquid surface determines the wavelength Λ of the observed surface wave. If the detection of the scattered light is in the plane of incidence in fact we have [9]:

$$\Lambda = \lambda_0/|\sin\theta - \sin\theta_0|, \qquad (2)$$

where θ_0 is the angle of incidence, θ the angle of observation and λ_0 the free space light wavelength.

For periodic damped surface waves energy conservation implies that the scattered light is a doublet of frequency $\Omega_0 \pm \omega$, where Ω_0 and ω are the angular frequencies of the incident light and the surface wave, respectively [9]. The scattered light together with part of the reflected light is detected by a photomultiplier. The resulting photocurrent containing the frequency difference between scattered and reflected light [10] is analysed by means of a heterodyne voltmeter. A typical example of a measured spectrum is depicted in fig. 1. Its peak is centered around f_0 = 1.010 MHz and the (full) width of the spectrum in excess of shot noise at half maximum is 150 kHz. Similar spectra have been measured at dif-
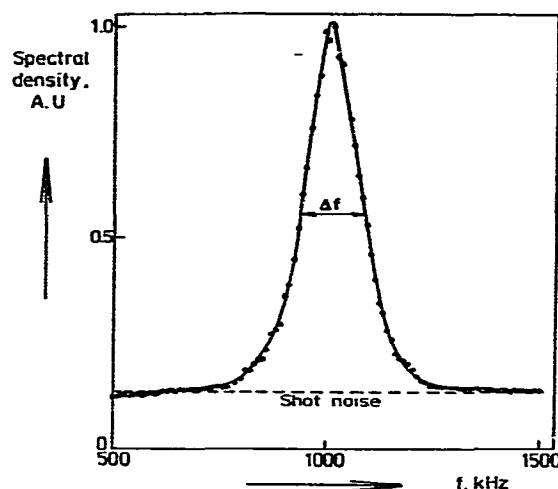
Fig. 1. Measured spectrum of the photocurrent fluctuations. Wavelength of the surface wave Λ = 30.9 μm (θ_0 = 60.03°, θ = 62.0° and λ_0 = 514.5 nm) and thickness of the film h = 48.5 nm. Peak position f_0 = 1.010 MHz and width Δf = 150 kHz.

ferent angles of observation θ in the range $2° \leqslant |\theta - \theta_0| \leqslant 6°$ corresponding to wavelengths 30.4 μm $\leqslant \Lambda \leqslant$ 10.3 μm when θ_0 = 60°.

In fig. 2 the resulting frequency shifts are plotted as a function of the wavenumber k (= $2\pi/\Lambda$) at constant film thickness. As can be seen clearly a linear relationship between f_0 and k exists in the range of k values investigated. According to eq. (1) the slope of the $f_0(k)$ versus k curve should be equal to $(\gamma/2\pi^2\rho h)^{1/2}$. A least squares fit through the measured data yields a slope of 5.8 m/s. Taking for ρ a value of 1000 kg/m^3 and for h a (measured) mean value of 48.5 nm one finds for the surface tension of the film γ = 32 mN/m. The surface tension of the solution from which the films were prepared, measured by means of a conventional method (drop weight method), appeared to be 35 mN/m at the same temperature where the light scattering experiments were carried out (300 K). A possible explanation for the 10% difference between the surface tensions could be found in refs. [11,6]. There dispersion relations for the stretching mode have been derived by using a more general electrohydrodynamic theory than the one leading to eq. (1). According to these theories a thermodynamically correctly defined surface ten-
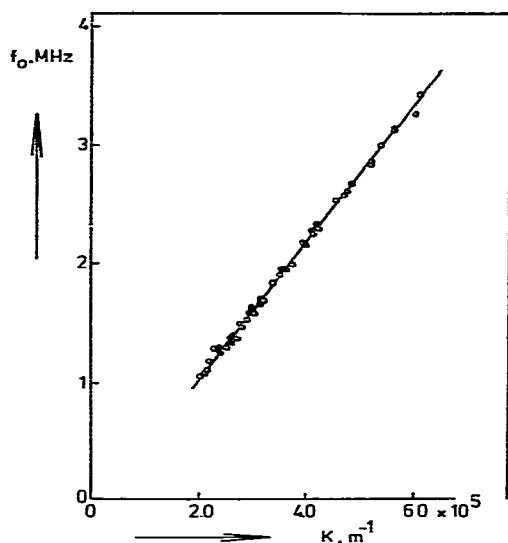
Fig. 2. Measured values of frequency shifts f_0 against k for two different films (o = film 1 and ● = film 2). The film thickness h = 48.5 ± 2 nm. The variation in thickness is due to small deviations during the measurements. The solid line is a least squares fit through all data.

sion should be used in interpreting the experimental data concerning the stretching mode. Actually the so-called double layer tension at constant volume [12] should be subtracted from the bulk value of the surface tension in order to find the tension that governs the oscillations of the stretching mode type of motion. This is a different, and more pronounced, effect than that which is measured in contact angle experiments as for example described by Princen and Frankel [13]. The difference between these effects depends basically on the thermodynamic conditions describing the experimental situations. A rough estimation [6] of this correction term for our films yields a decrease of about 3 mN/m with respect to the bulk value for the surface tension. As far as the widths of the measured spectra is concerned it appears that the width is mainly determined by the divergence of the laser beam and the geometry of our optical system: no reliable conclusions concerning the film properties can be subtracted from these data thus far.

Summarizing we may conclude that by laser intensity fluctuation spectroscopy spectral densities up to the MHz range can be measured and that valuable

information can be extracted from the spectra. Furthermore it appears that dispersion relations derived on the basis of macroscopic theories can be applied in the surface wavelength region considered. The surface tension found from these high frequency experiments is approximately equal to the static value, at least in the k and h region described here, and the observed small deviations can be explained by the influence of the interaction forces on the dynamics of the surface waves. A detailed discussion of experimental and theoretical results will be presented elsewhere.

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