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Dynamic light scattering from colloidal monolayers

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Abstract. Quasi-elastic light scattering has been used to investigate the viscoelastic properties of colloidal monolayers on the surface of water. The frequency shifts, linewidths and intensities of the scattered light demonstrate that it arises from thermally excited capillary waves on the liquid surface. The photon correlation functions are consistent with predictions for a surface monolayer, and have been analysed in terms of the tension and dilational modulus of the surface. The measured values of the associated surface viscosities were compatible with zero. The π - A variation was in accord with literature data from Wilhelmy plate measurements. However, at small A the light scattering values of the dilational modulus systematically exceeded those derived from the π - A isotherm. This is as expected for viscoelastic relaxation in the monolayer on time scales much slower than the inverse wave frequencies.

1. Introduction

Colloidal particles, having sizes between 1 nm and 1 μm , occur widely in nature and have many practical applications. In particular the presence of such particles at a liquid surface or interface may drastically affect its physical properties. Such colloidal monolayers are widespread, appearing in such diverse technological fields as enhanced oil recovery, detergency and food manufacture. Model colloid systems are useful in physical experimental studies: for example polystyrene microspheres can be trapped at the surface of a liquid [1, 2], forming an array of monodisperse charged particles. This provides a rather well defined two-dimensional model system in which the inter-particle interactions are, in principle, exactly known, permitting well controlled experiments. The present study is an investigation of the viscoelastic properties of an air/water interface stabilised by such a colloidal monolayer.

Light scattering from thermally excited capillary waves at liquid surfaces has become an accepted method of investigation of surface properties [3, 4]. The particles in such a colloidal monolayer are of size comparable with the wavelength of light. In the present work monodisperse 1.088 μm diameter particles were trapped at the surface, separated by distances which were varied from about 1 to 3 μm , much less than the wavelength of the capillary waves ($\sim 100 \mu\text{m}$). The system thus comprised a relatively dense array of particles, which were very large compared with the RMS amplitude of the thermal ripples ($\sim \text{\AA}$). It is not clear that scattering from the surface waves would be observable in the presence of such gross inhomogeneities at the surface. The particulate nature of the monolayer might be expected to dominate the scattering of light in such a system (cf [5]). The present results, however, indicate that this is not the

case, at least as regards the time dependence of the scattered intensity. Quasi-elastic scattering from the dynamic surface fluctuations can indeed be detected, providing a useful probe of the viscoelastic properties of a colloidal monolayer.

2. Theoretical background

The capillary fluctuations of a surface may, in principle, be affected by up to four surface properties. The waves are directly influenced by the surface tension (γ), and indirectly by the dilational modulus of the surface (ε). The latter corresponds to the conventional dilational modulus of a monolayer:

$$\varepsilon = -A \frac{d\pi}{dA}. \quad (1)$$

where π is the surface pressure, and A the area per particle. However, the capillary waves are affected by a value of ε appropriate to the wave frequency ($\varepsilon_0(\omega)$), whereas (1) defines the equilibrium value for $\omega \rightarrow 0$ ($\varepsilon_0(\text{eq})$). The effects of ε upon the transverse or capillary waves arise from coupling to longitudinal or compression fluctuations in the monolayer.

The strains governed by both γ and ε may involve dissipation of energy: the corresponding surface viscosities γ' and ε' can be incorporated by expanding the moduli as positive definite response functions:

$$\gamma = \gamma_0 + i\omega\gamma' \quad (2)$$

$$\varepsilon = \varepsilon_0 + i\omega\varepsilon'. \quad (3)$$

γ' and ε' affect shear transverse to the surface and dilation in the surface plane respectively [6]. It should be noted that neither is the conventional surface viscosity, which governs shear *in* the surface plane.

The propagation of capillary waves on a surface supporting a colloidal monolayer has not been investigated before, either experimentally or theoretically. We will use the theoretical description of a liquid surface supporting a molecular monolayer. This essentially assumes that the surface properties involved are macroscopic properties of the system, and are not directly caused by the microscopic nature of the monolayer. The appropriate dispersion equation is then [3]:

$$D(\omega) = [\varepsilon q^2 + i\omega(m + q)][\gamma q^2 + i\omega\eta(m + q) - \omega^2\rho/q] - [i\omega\eta(q - m)]^2 = 0. \quad (4)$$

Here ω ($= \omega_0 + i\Gamma$) is the complex propagation frequency of a capillary wave of real wavenumber q , η and ρ are respectively the viscosity and density of the fluid supporting the monolayer and

$$m = \sqrt{q^2 + i\omega\rho/\eta} \quad \text{Re}(m) > 0. \quad (5)$$

Again we use the spectrum of light scattered by thermally excited capillary waves for a molecular film [3], $P(\omega|X)$ where X is the set of surface properties involved: it is not necessary to state the explicit form here.

Determination of ω requires numerical solution of the dispersion equation, but approximations are available. To first order the frequency and damping depend only upon the surface tension and viscosity of the liquid [3]:

$$\omega_0^2 \approx \frac{\gamma q^3}{\rho} \quad (6)$$

$$\Gamma \approx 2 \frac{\eta q^2}{\rho}. \quad (7)$$

Agreement of the experimental values of ω_0 and Γ with these relations can be taken as identifying the nature of the scattering process.

3. Experimental methods

The colloidal particles were monodisperse polystyrene spheres (diameter 1.088 μm , SD = 0.079 μm). They are inherently negatively charged due to covalently bonded surface sulphate groups. They were cleaned using mixed-bed ion-exchange resins and re-suspended in methanol. The ion-exchange resin will strip all water soluble ions and adsorbed surfactant from the latex, and convert the acid groups on the particles to the hydrogen form. The final surface charge density, determined by conductometric titration, was 4 $\mu\text{C cm}^{-2}$ ($\pm 10\%$).

Colloidal monolayers were formed by carefully delivering a known amount of the methanol-latex suspension of given concentration to the liquid surface using an Agla syringe. The suspension spread rapidly and evenly across the entire surface area. The methanol evaporated readily and no problems of penetration into the bulk liquid were observed. It was found that the best monolayers were obtained when the aqueous subphase was slightly salty (10^{-3} M NaCl). The expanded monolayers were often slightly inhomogeneous, but contained large, irregular regions about one third of the trough area which were very homogeneous, and between which the particle density only varied by $\sim 10\%$. The area illuminated by the laser beam was very much smaller than these regions, so that the observations essentially pertain to a uniform monolayer. The monolayer was allowed to equilibrate for 100 min before light scattering experiments were initiated.

The monolayers were spread on the surface of the aqueous subphase contained in a PTFE Langmuir trough with a glass window in its base, mounted on an inverted optical microscope for visual observation. The trough had a movable PTFE barrier for monolayer compression. The PTFE tended to acquire an electrostatic charge which was discharged before an experiment. The trough was thermostatted at $21.9 \pm 0.2^\circ\text{C}$ for the present experiments. The entire apparatus was on a vibration-isolated optical table.

A conventional surface light scattering spectrometer [7] was constructed around this apparatus. The light from a HeNe laser (25 mW, $\lambda = 633$ nm, TEM₀₀ mode) was spatially filtered to ensure a Gaussian intensity profile and directed onto the liquid surface. The beam was incident upon the surface at 45.3° with a diameter ~ 2 mm. Heterodyne detection of the scattered light is necessary to determine the rather small frequency shifts of light scattered by capillary waves. Several reference beams at the frequency of the original laser light were generated by a diffraction grating placed before, and imaged at the liquid surface. These reference beams diverged from

the surface at various small angles ($< 1^\circ$) from the specular reflection, mixing with light scattered by thermally excited capillary waves. An aperture in front of the photodetector selected one of the reference beams, together with its accompanying scattered light, for detection. The photomultiplier output was analysed by photon correlation: a typical correlation function recorded for a colloidal monolayer is shown in figure 1. At each monolayer area examined ten successive correlation functions were recorded after the monolayer had been allowed to equilibrate for 5–10 min; the function shown is the average of such a data set.

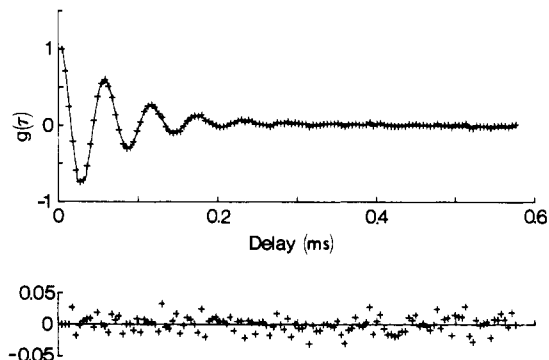


Figure 1. A correlation function ($q = 552.8 \text{ cm}^{-1}$) observed for a colloidal monolayer at $A = 3.20 \text{ } \mu\text{m}^2$ per particle. The line is the best-fit function of the form of (9). The residuals of the fit are randomly distributed about zero. The noise on the correlation function (RMS value of the residuals) is 1.3% of the amplitude of the time dependent part of the correlation function.

Two methods have been used to analyse these data. The first, yielding unbiased estimates of the wave frequency and damping [7], involved least-squares fitting with the objective function

$$g(\tau) = b + a \cos(\omega_0|\tau| + \phi) \exp(-\Gamma\tau) \exp(-\beta^2\tau^2/4). \quad (8)$$

Here b and a are background and amplitude factors, while the phase term ϕ allows for deviations of the spectrum of the scattered light from a Lorentzian form. The final Gaussian term represents an instrumental line-broadening function.

The values of ω_0 and Γ thus found may depend on up to four physical quantities (γ and ε), supposing the viscosity and density of the subphase to be known. It is not possible to infer four physical properties from only two observables without invoking either extra information or possibly unjustifiable assumptions.

The second method of analysis therefore involved fitting the observed correlation functions with an objective function directly based upon the theoretical spectrum of the thermally excited capillary waves on a liquid surface supporting a monolayer:

$$g(\tau) = b + a \text{FT}\{P(\omega|X)\} \exp(-\beta^2\tau^2/4). \quad (9)$$

Recall that X represents the four surface properties: γ_0 , γ' , ε_0 and ε' . In computing this functional form η and ρ were taken to have their accepted values for the subphase. This direct method of data analysis has been successfully tested on molecular monolayers [4, 10] and a detailed description has been published [11]. The line in figure 1

is for such a fit—the randomness of the residuals indicates the appropriateness of the functional form.

The relative intensities of both the scattered light and the reference beam can be determined from the fitted values of a and b together with the mean photon count rate [8]. The scattered intensity thus determined relates to the fluctuations giving rise to the time dependence of the observed correlation functions, and so depends upon the nature of these fluctuations. For thermally excited capillary waves it is predicted that $I_s \propto q^{-2}$ [3], providing a method to check the thermal origin of these fluctuations.

4. Results and discussion

We present here typical results for one monolayer: they are quantitatively supported by data for other monolayers. Light scattering observations were made as the monolayer was compressed from 8 to 2 μm^2 per particle. It was found that the surface pressure of the monolayer had risen considerably by the latter area, even though it exceeds the area per particle for a compact lattice of particles ($A \approx 1 \mu\text{m}^2$). The difference presumably arises from interparticle electrostatic repulsion [9]. Observations were also made on re-expansion; the results are not shown but were in good agreement with the data from the compression run. The observed correlation functions were first analysed to yield the complex wave frequency ω , and then directly in terms of the surface properties of interest.

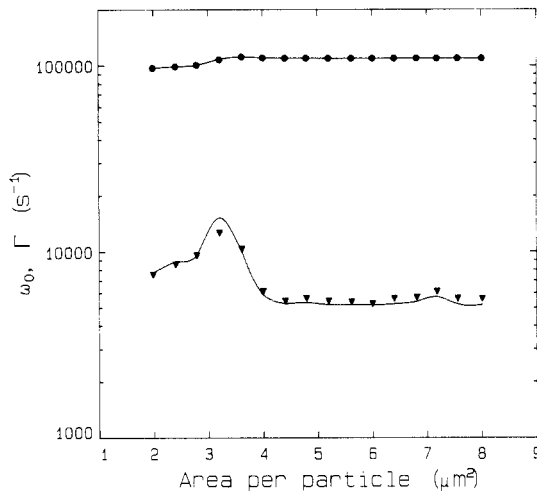


Figure 2. The frequency (\bullet) and damping (\blacktriangledown) of capillary waves of $q = 552.8 \text{ cm}^{-1}$ as functions of the area per particle in the colloidal monolayer. The lines and the errors on the data are discussed in the text.

4.1. Capillary wave propagation

The measured ω_0 and Γ values determined from correlation functions at $q = 552.8 \text{ cm}^{-1}$ are shown in figure 2 as functions of the area per particle. The lines on the figure will be discussed below. The errors on ω_0 , estimated by taking the standard deviations of the values for the ten individual correlation functions recorded at

each A , increased from 0.17 to 0.34% as the surface pressure rose. The errors on Γ were about 7.5%, basically independent of A .

During the compression run light scattering observations were made for several q values at certain selected areas. The range of q covered was limited, but these data confirm the nature of the fluctuations from which the light is scattered. ω_0 and Γ for one particular area are shown in figure 3. The best power law fits have exponents of 1.49 ± 0.03 for frequency and 1.96 ± 0.08 for damping, in excellent agreement with the expected values of 1.5 and 2.0 respectively (equations (6) and (7)). Similar data at other areas confirmed these results.

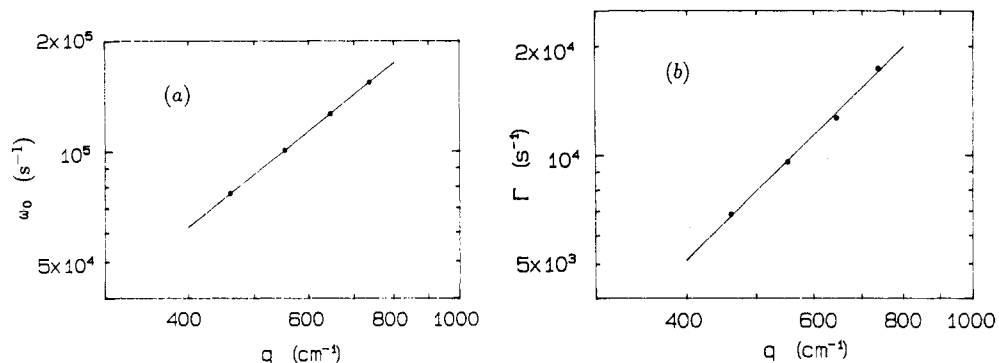


Figure 3. Logarithmic plots of the q variations of (a) ω_0 and (b) Γ for a colloidal monolayer at $A = 2.79 \mu\text{m}^2$ per particle. The lines shown are the best-fit power law dependences.

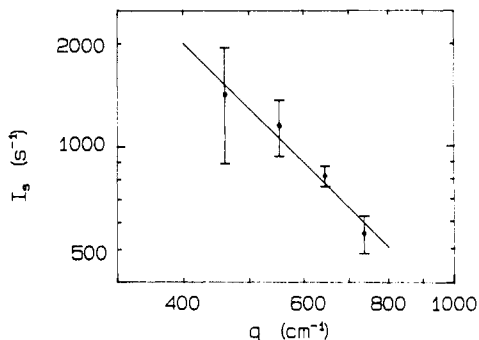


Figure 4. The q dependence of the intensity of light scattered by a colloidal monolayer ($A = 3.6 \mu\text{m}^2$). The line is the best-fit power law variation.

Figure 4 shows the q variation of I_s . The errors are large, but the best power law dependence, of exponent -1.99 ± 0.28 , agrees well with the expected q^{-2} behaviour. Over this range of q the heterodyne reference beam intensity remained roughly constant. Data for different areas per particle and for several other monolayers supported this conclusion.

These observations confirm that the quasi-elastic surface light scattering indeed arises from thermally excited capillary waves.

4.2. Surface properties

The data were then analysed, using the objective function of equation (9), directly in terms of the surface viscoelastic properties of the colloidal monolayer. In the present case, the two surface viscosities were found to be essentially zero at all A . One or two very small non-zero values were found, but they were compatible with zero within the errors. The surface pressures and values of the dilational modulus thus found are shown in figures 5 and 6.

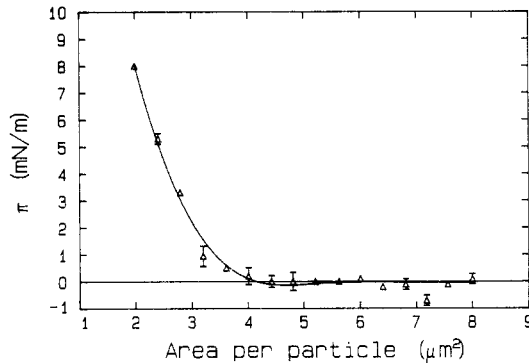


Figure 5. π - A behaviour determined from the same light scattering data as figure 2. The line is a cubic spline fit to the data. See text for details.

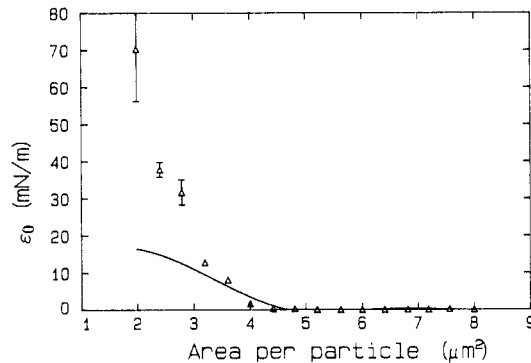


Figure 6. The dilational modulus as a function of area per particle for the same monolayer as figure 5. The line is the logarithmic derivative of the spline fit of that figure, representing the variation of the equilibrium modulus ϵ_0 (eq).

The *form* of the observed π - A variation, and the magnitudes of π broadly agree with literature data from classical manometry [12, 13]. Detailed comparisons would be misleading, as the exact results will depend upon the size, charge state and nature of the colloidal particles.

The consistency of the surface properties with the observed capillary wave propagation can be checked. Using the surface properties from the direct fitting (figures 5 and 6, together with the fitted values of the surface viscosities where these differed from zero) the dispersion equation (equation (4)) was solved for the complex wave

frequency. The lines in figure 2 represent the variations of ω_0 and Γ thus determined: the general forms accord well with the observed results. The frequencies agree excellently—the RMS deviation is 0.18%, in accord with the error quoted above. The agreement of the two sets of Γ values is, as expected, rather poorer. However, whilst there might appear to be systematic differences, the runs test [14] suggests that the deviations are consistent with the hypothesis of randomness at the 5% significance level. The RMS deviation (6.8%) again agrees with the error previously cited.

4.3. Viscoelastic relaxation

Now, at low frequencies of applied stress the elastic modulus ε_0 corresponds to the dilational modulus of the monolayer. This classical or equilibrium value $\varepsilon_0(\text{eq})$ can be estimated from the logarithmic derivative of the variation of surface pressure with A (equation (1)). To this end the observed π - A variation was approximated by a cubic B-spline function, as shown in figure 5. The variation of $\varepsilon_0(\text{eq})$ calculated from the derivative of this spline is shown in figure 6. The exact variation is, of course, dependent upon the details of the spline fit to the π - A data. The broad conclusions were, however, not altered by quite marked changes to this curve.

For areas $\gtrsim 3.6 \mu\text{m}^2$ per particle the agreement of $\varepsilon_0(\omega)$ with $\varepsilon_0(\text{eq})$ is very good, whereas this is not so for $A < 3.6 \mu\text{m}^2$. The observed values of $\varepsilon_0(\omega)$ at these areas are inconsistent with the π - A isotherm. The variation of π can be extrapolated from the smallest area at which $\varepsilon_0(\omega) \approx \varepsilon_0(\text{eq})$ by integration of (1) using the $\varepsilon_0(\omega)$ values. This leads to values of π which clearly exceed those observed, rising to 27.5 mN m^{-1} at $A = 2.0 \mu\text{m}^2$.

This inconsistency of $\varepsilon_0(\omega)$ and $\varepsilon_0(\text{eq})$ is not due to inadequate equilibration of the monolayer, as similar values of π and $\varepsilon_0(\omega)$ were obtained during re-expansion. Quantitatively similar data were also observed in different experiments involving different equilibration times. The differences are well outside the errors of determination of $\varepsilon_0(\omega)$, even though large values of this modulus are not well determined by light scattering.

We conclude that the discrepancies of figure 6 at low A are real, indicating that viscoelastic relaxation of the modulus ε has occurred. The frequency dependence of ε is unknown, but, in general for viscoelastic relaxation, increasing the frequency of the perturbation involved causes the viscous part of a viscoelastic modulus to fall whilst the elastic part rises from its low-frequency value. In the present case, by the time ω_0 has been reached, the (non-zero) low-frequency dilational viscosity, ε' , has evidently relaxed to an undetectable value, transforming into part of the elastic modulus $\varepsilon_0(\omega)$. The differences between our estimates of $\varepsilon_0(\text{eq})$ and $\varepsilon_0(\omega)$ provide an estimate of the strength of the relaxation process involved: this varies with A , increasing from 4 mN m^{-1} at $A = 3.2 \mu\text{m}^2$ to about 54 mN m^{-1} for $A = 2.0 \mu\text{m}^2$. We know of no low-frequency measurements of the dilational viscosity of colloidal monolayers so that detailed speculation about the relaxation would be premature. However, it is possible to conclude from the small values of the viscosity ε' at the present capillary wave frequencies ($\omega_0 \sim 10^5$) that the time scale associated with the relaxation must be $\gg 1/\omega_0$.

5. Conclusions

For the first time light scattering has been used to investigate the viscoelastic properties of a liquid surface supporting a colloidal monolayer. The presence on the surface

of particles of size about the wavelength of light does not seem to perturb the quasi-elastic scattering of light by capillary waves, as shown by the observed q dependence of the measured ω_0 and Γ values. The variation of the scattered intensity with q^{-2} confirms the thermal origin of the fluctuations involved. The measured propagation of the capillary waves is in accord with that predicted on the basis of the surface viscoelastic properties inferred from the light scattering data. At the capillary wave frequencies the two accessible surface viscosities are of negligible magnitude. However at low areas per particle the high-frequency value of the dilational elastic modulus from the light scattering data systematically exceeds that deduced from the π - A plot, indicating that the modulus ϵ is subject to viscoelastic relaxation.

Why do the large surface inhomogeneities not affect the quasi-elastic scattering of light by thermally excited capillary waves of much smaller amplitudes? Microscopic observation of the colloidal particles on the surface reveals Brownian motion about their mean positions. But the long timescale of these motions implies that the consequent Doppler shifts of reflected light will be very small compared with ω_0 : the particles are essentially static on the timescales of the capillary fluctuations. Such nearly elastically scattered light will not confuse the spectrum due to the capillary waves: the scattering due to the array of colloidal particles will here just increase the flare contribution to the heterodyne reference beam at the detector. This Mie scattering will exhibit a q dependence which reflects the spatial distribution of particles within the surface plane. For a regular surface monolayer the intensity scattered would be almost independent of q except at those high q values corresponding to one or two particle separations. More detailed discussion would not be warranted as the effects are restricted to the reference beam intensity.

The particles are very effectively trapped at the surface [1, 2], the potential well being $> 10^6 kT$ deep: the particles follow the motions of the surface. The particles can be considered as attached to the surface extremities of fluid streamlines [15], so that their vertical motions are just part of the overall surface movement. The capillary waves involve the entire interfacial system, and thus changes in scattering by the particles due to their following of the surface will just be subsumed into the surface wave scattering (cf [5]).

Dynamic light scattering thus provides a useful, non-perturbative probe of these important but fragile systems. The technique can provide information not obtainable by conventional surface methods, which may be useful in the investigation of inter-particle interactions.

Acknowledgments

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