



Experiment title: Influence of surface tension, viscosity and surface rigidity on the capillary wave spectrum of complex fluids

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SI-1083

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Report:

Monolayers of organic surfactants are of interest for potential industrial applications. The organic films can be transferred onto solid substrates in a very elegant way by using the Langmuir Blodgett technique. However, the actual organisation of the monolayers takes place on a liquid surface (Langmuir monolayers), where the organisation of individual molecules is hampered by the presence of thermally excited capillary waves. Recently Langmuir monolayers have been prepared and investigated on the surface of complex fluids, in order to make use of the special stiffening properties of this subphase that dampes the capillary waves. Using organic surfactants with a positive charge in the headgroups and aqueous suspensions of disc-like nanoparticles (sols) with a negative surface charge, a hybrid layer consisting of an adsorption monolayer of nanoparticles underneath the surfactant monolayer is formed. GIXD investigations of these systems have revealed a reduced Debye-Waller factor for the Bragg reflections originating from the surfactant layer [1]. The surface hybrid-layer was found to be macroscopically stable and glassy-like and able to carry macroscopic water droplets of milimeter dimensions despite its own thickness of only about 50nm [2]. Although these results point towards an increase of net-intermolecular van der Waals interaction, probably caused by a reduction of fluctuations within the layer, direct information about the (surface) dynamic is generally not obtainable from static measurements. To adress this question, we have measured and compared the dynamics of free and monolayer covered water and sol surfaces by means of XPCS. In order to establish surface sensitivity, measurements were performed under grazing incidence conditions. The wavevector transfer $q_{||}$ parallel to the liquid sample surface was typically in the range between 300 and 600 cm^{-1} , corresponding to probed lateral length scales ranging from 100 to 200 μm . The recorded correlation functions were divided by the correlation function at the specular position ($q_{||}=0$) to eliminate sample independent fluctuations. The sample environment consisted of an aluminum trough (90mm diameter, 500 μm depth) in a housing which was flushed with H_2O saturated helium to minimise parasitic air scattering. Monolayers of the phospholipid 1,2-dipalmitoyl-phosphatidyl-choline (DPPC) were prepared by spreading

from a chloroform solution at 0.2g/L concentration using a Hamilton Microsyringe. The amount of solution needed to reach a certain surface pressure had been calculated from calibration pressure/area isotherms measured on a conventional Langmuir trough. This procedure had been proven to provide a precision better than $\pm 2\text{mN/m}$. The sol subphases were prepared by dissolving 2.4wt.% of synthetic clay nanoparticles (Laponite RD) in ultrapure water. The mass density of these aqueous suspensions was determined as 1.01g/cm^3 . Measurements of the surface tension using a conventional tensiometer (Nima ST 9005) yield values of about 73.5mN/m using Wilhelmy plate and du Nouy ring measuring geometries. The bulk shear viscosity of the sols was determined by rheology experiments [1] and yield a value of $\eta=2.2\text{mPas}$. Capillary waves are characterised by the wavevector $q_{||}$ and their complex frequency $\omega=\omega_0+i\Gamma$, where ω_0 is the propagation frequency of the wave and Γ represents the damping. For simple newtonian liquids like water, the dispersion relation in first order approximation is given by

$$(1) \quad \omega_0 = \sqrt{\frac{\sigma_0 q_{||}^3}{\rho}},$$

where σ_0 is the surface tension of the liquid and ρ is its mass density. The damping constant Γ is in this case given by

$$(2) \quad \Gamma = \frac{2\eta q_{||}^2}{\rho},$$

where η is the viscosity of the liquid. While the values for ω_0 obtained in previous experiments were found to be in excellent agreement with the theoretical prediction, the damping constants obtained were found to be too high, resulting in unrealistic high values for η [3]. Recent developments in the theoretical understanding [4] of these observations suggested that resolution effects have to be taken into account. The related resolution parameters are only dependent on the experimental setup and not on particular sample properties. They can therefore be determined using reference samples of which all physical parameters (σ_0 , ρ , η) are known from independent macroscopic measurements.

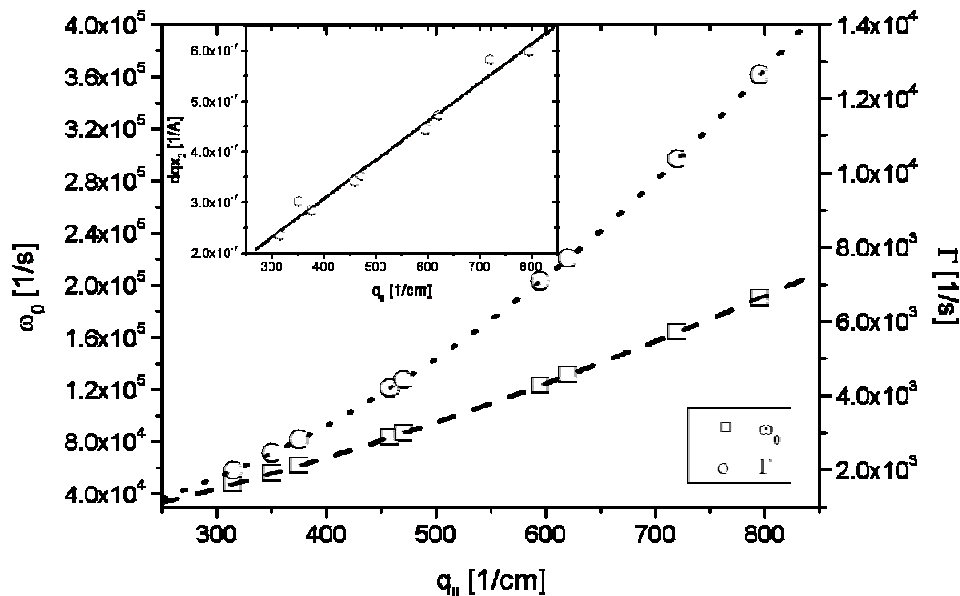


Fig. 1 Propagation frequency ω_0 and damping constant Γ for pure water as a function of $q_{||}$. The inset shows the values found for the resolution parameter dq_{x_2} , obtained from modeling the correlation functions for pure water using the known values for surface tension, mass density and viscosity.

Figure 1 shows the propagation frequency ω_0 and the damping constant Γ for pure water. The inset in Figure 1 displays the values obtained for the resolution parameter dq_{x_2} versus $q_{||}$. The data points approximate linear behaviour over the investigated $q_{||}$ -range. The solid line represents a linear fit of the data and the resulting function $dq_{x_2}(q_{||})$ was used to determine the parameter dq_{x_2} for any given $q_{||}$ under investigation. The most striking difference in the correlation functions for the pure and monolayer covered water and sol surfaces is the change from a heterodyne to a homodyne signal. Two typical correlation functions are shown in Figure 2.

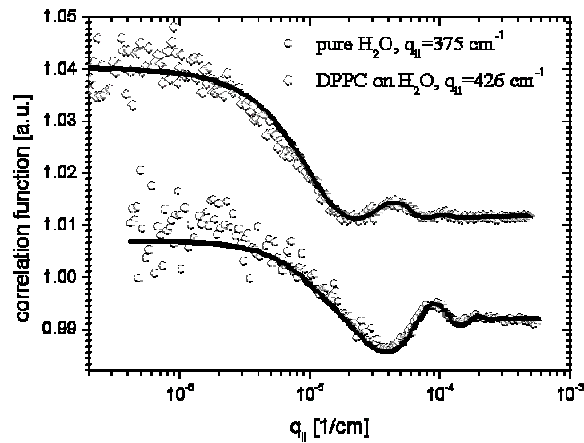


Fig. 2 Typical correlation functions for the pure and monolayer covered water surface. It strikes out, that the signal is changing from heterodyne (pure water) to homodyne in the presence of the DPPC monolayer with a surface pressure of 35mN/m. Solid lines are theoretical curves according to a model of propagating capillary waves, accounting for resolution effects.

It has been shown recently [4], that for given sample parameters and parallel wavevector transfer $q_{||}$ the transition from heterodyne to homodyne is a coherence effect, depending only upon the resolution and not upon the sample. Using the resolution parameters known from the reference measurements of the free water surface, the transition from heterodyne to homodyne was also observed in the calculated curves. However, for a DPPC monolayer on water at a surface pressure of 35mN/m an increased viscosity was found over the whole investigated $q_{||}$ -range, resulting in a larger damping constant Γ in comparison to pure water. The damping of capillary waves in the presence of insoluble monolayers is a well known phenomena [5]. A simple theory by Levich [5] introduces the elastic constant (ε) of the monolayer to qualitatively describe the phenomenon. The damping constant Γ becomes, within this theoretical framework, a function of ω_0 , η , ρ , $q_{||}$ and ε . Although there are other theories available, which pay more attention to the details of interaction in the monolayer, the theory of Levich is nevertheless appealing, as it introduces with ε only one unknown parameter that can be therefore determined to a satisfactory level of confidence.

Figure 3 shows the damping constants found for DPPC monolayers on water at a surface pressure of 35mN/m, the damping constants for pure water are also shown for comparison purposes. The dashed line represents the damping constant according to Levich's theory. The $q_{||}$ -dependence as well as the absolute values are in excellent agreement with the data for $\varepsilon \approx 0.019$ mN/m. The inset in Figure 3 displays the propagation frequencies for the case of pure water and in the presence of the DPPC monolayer with 35mN/m surface pressure. The surface pressure (π) is defined as $\pi = \sigma_0 - \sigma$, where σ_0 is the surface tension of the free subphase surface and σ is the actual surface tension in the presence of the monolayer. The actual surface tension of the system can therefore be calculated as $\sigma = \sigma_0 - \pi$, using the known surface tension of the free subphases (72.8mN/m for water and 73.5mN/m for a sol with 2.4wt.% mineral content). The propagation frequency of the capillary waves is found to be reduced in the presence of the monolayer, compared to the free water surface. The dashed line in the inset of Figure 3 was created according to equation (1), using the actual surface tension σ . It is noteworthy that with known values for σ_0 and π there is no free parameter in the calculation, which nevertheless exhibits excellent agreement with the data. In the presence of an insoluble monolayer, the damping of the capillary waves is increased, while their propagation frequency is decreased. The damping constants for a pure sol with 2.4wt.% mineral content and a sol with the same concentration but covered by a DPPC monolayer at a surface pressure of 45mN/m are depicted in Figure 4. As already mentioned, all physical parameters for the pure sol were already known from macroscopic measurements. The obtained correlation functions were well described by these parameters in conjunction with the resolution parameters determined by the measurements of pure water. Hence apart from background and contrast there were no free parameters.

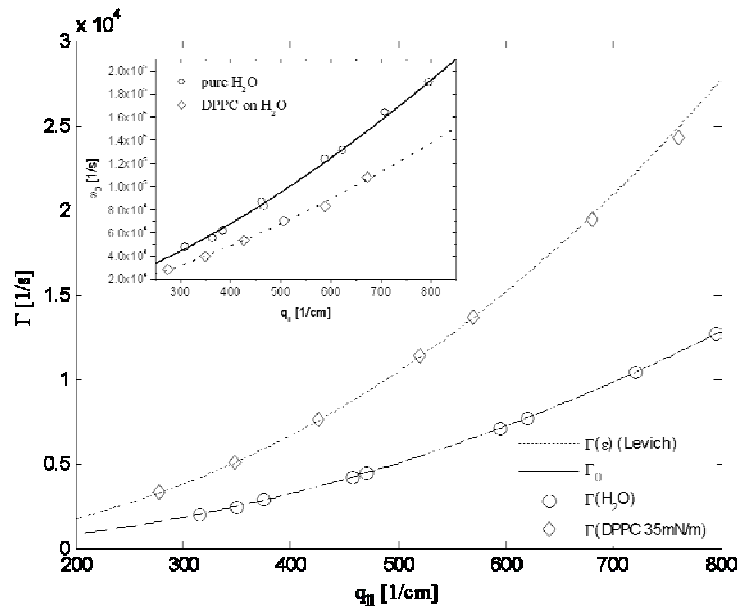


Fig. 3 Damping constants for the free and monolayer covered (DPPC $\pi=35\text{mN/m}$) water surface. The solid line is representing the theoretical values in the case of pure water and was calculated according to equation (1). The dotted line represents the theoretical progression in the case for the monolayer covered water surface and was obtained from Levich's theory by optimisation of the parameter ε . Inset: propagation frequencies for the above mentioned systems. Theoretical curves were obtained by applying equation (1), using the surface tension σ_0 in the case of pure water and the effective surface tension σ in the presence of the monolayer, respectively.

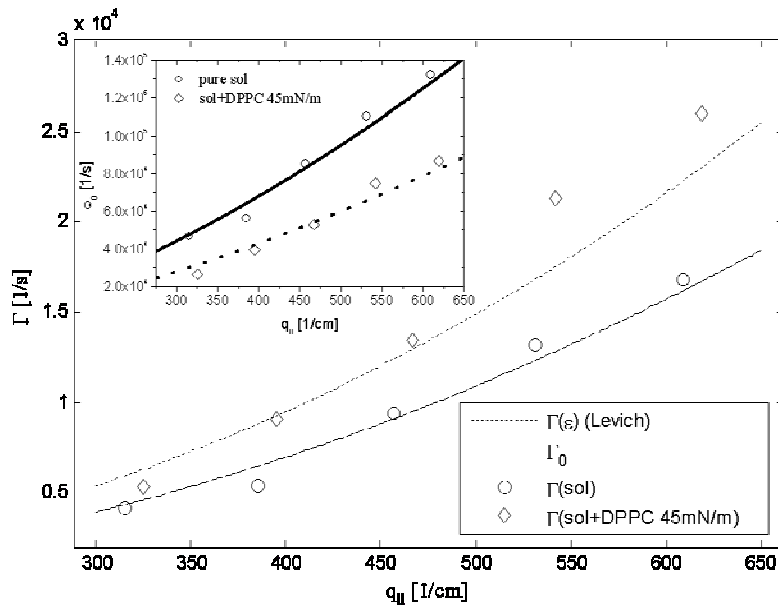


Fig. 4 Damping constants for the free and monolayer covered (DPPC, $\pi=45\text{mN/m}$) sol surface (2.4wt.% mineral content). Applying the resolution parameters fixed by the measurements of pure water, there is in the case of the pure sol no adjustable parameter neither in the modeling of the correlation functions nor in the theoretical curve for Γ_0 according to equation (2). Inset: The corresponding propagation frequencies, theoretical curves were created using equation (1) with σ_0 and σ for the pure and monolayer covered sol systems respectively.

The reasonable agreement between the data and the calculated curves can serve as a confirmation of the validity of the resolution parameters*. As in the case of water as a subphase, the damping constant is increased in the presence of the lipid-mineral hybridlayer. However, the increase in the viscosity as determined from the correlation functions are less distinct than in the case of a water subphase, leading to damping constants that are closer to those of the pure sol. Consequently, the value for ε obtained by fitting

* The pure water was the first sample measured during the beamtime, while the pure sol was the last one. The agreement of the resolution parameters found, confirm that these parameters are indeed stable parameters for a given beamline setup.

the damping constants to the Levich model is also smaller (0.017mN/m). Taking into account that ϵ is somehow inversely proportional to the compressibility of the surfactant layer [6], this result is in good agreement with the measurements of the reference pressure/area isotherms (not shown) where indeed the compressibility in the region of interest was found to be larger in the case of a sol subphase compared to a water one. The specific damping properties of the nanoparticles adsorbed to the organic monolayer, as attributed from static measurements are most likely most effective on length scales comparable to the particle size in the order of 25nm. However, at a higher surface pressure of 58mN/m, where the hybridlayer was found to be macroscopically stiff and glassy-like [2], there is evidence that the capillary waves even on the experimentally accessible length scales become overdamped.

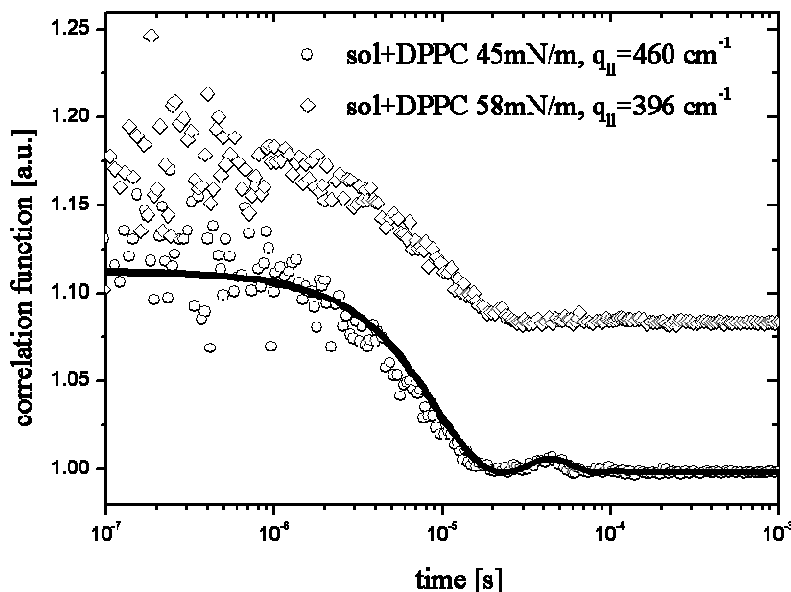


Fig. 5 Typical correlation functions for DPPC monolayers on sol surfaces at surface pressures of 45 and 58 mN/m respectively. At the higher surface pressure, there is evidence for an overdamping of the capillary waves. The corresponding correlation functions show barely any features except for an exponential-like decay.

Figure 5 shows a comparison between two typical correlation functions for DPPC monolayers on a sol subphase at surface pressures of 45 and 58mN/m respectively. At the higher surface pressure, the correlation function only shows an exponential-like decay. The absence of a hump in the region between 10^{-5} and 10^{-4} s is indicative of the absence of propagating capillary waves at the sample surface.

In conclusion we have successfully measured the dispersion relations of free and monolayer covered water and sol surfaces. Data analysis and interpretation crucially benefitted from the determination of setup dependend resolution parameters by measurements of reference samples with known physical properties. In the presence of the surfactant monolayer, the propagation frequency of the capillary waves is generally decreased, while their damping is increased. Applying a simple theoretical approach, the increase in the damping constant was successfully related to properties of the monolayer by the introduction of an elastic constant. At high surface pressure, evidence for an overdamped behaviour of the capillary waves at the sample surface was found for the sol system. This finding is in agreement with previous interpretations of the micro- and macroscopic properties of these hybrid layers from static measurements.

Further data analysis and a manuscript for peer review are in progress.

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