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Ripplon Spectroscopic Study of Surface Viscoelasticity of Water with Piston Oil

単分子膜を展開した液体表面粘弾性のリプロンによる観察

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1. Introduction

Ripplon spectroscopy is a useful technique to investigate the molecular dynamics at the liquid surface and liquid-liquid surface. Ripplon is a thermally excited capillary wave, whose velocity and damping are determined by the surface tension and shear viscosity of the liquid. In addition for the liquid surface covered with a molecular layer, the ripplon propagation is modified also by the surface viscoelastic properties of the layer. In this study, we carried out the measurement of the surface viscoelastcity of the molecular layer formed by the piston oil.

2. Observation of compressive surface layer by ripplon light scattering

We can prepare quite stable mono-molecular layer by injecting a drop of piston oil on to pure water surface; a molecular layer spontaneously expands and the rest are condensed into a droplet floating on the surface and the surface pressure is kept constant. The piston oil is used, therefore, to compress a Langmuir film at a constant surface pressure in the fabrication process of LB films. It is a kind of coexistence of the two- and three-dimensional phases and we can expect some relaxation phenomenon since it should take a finite time to undergo the transition. The purpose of the study is to determine the high frequency limit of the relaxation parameters by observing the ripplon propagation in MHz region.

The details of the ripplon light scattering system have already been reported[1)], and we briefly explain the principle. The light incident to the liquid surface is diffracted by the periodical surface deformation of the ripplon and the wavenumber of ripplon to be observed is determined by the Bragg condition,

$$k = K \sin\theta$$

where k and K are the wave numbers of the ripplon anf the incident light, respectively, and θ is the scattering angle. The scattering by the propagating ripplon shifts the frequency of the light through the Doppler effect and the relation is expressed as,

$$\omega_0 = \omega_s - \omega_i$$

where ω_0, ω_s, ω_i are the angular frequency of the ripplon, scattered light, and the incident light, respectively. We can observe the ripplon power spectrum by analyzing the spectrum of the scattered light with the optical heterodyne technique. The angular frequency ω_0 and the damping constant Γ of the ripplon are approximately given by

$$\omega_0 = (\sigma/\rho)^{1/2} k^{1/3}$$
$$\Gamma = 2(\eta/\rho)k^2$$

where σ is surface tension, η and ρ are the viscosity and density of liquid, respectively.
For the surface with visco-elastic layer, the ripplon propagation is modified and the power spectrum of the ripplon is given by[2)]

$$P(\omega) = \frac{k_B T \rho}{4\pi\omega\eta^2 k} \mathrm{Im}\left\{ \frac{S^2 + (\alpha y + \beta S)\left(\sqrt{1+2S} - 1\right)}{D(S)} \right\} \quad (1)$$

$$D(S) = S^2\left[(1+S)^2 + y - \sqrt{1+2S}\right] + (\alpha y + \beta S)\left[S^2\sqrt{1+2S} + y\left(\sqrt{1+2S} - 1\right)\right] \quad (2)$$

where $y = \sigma\rho/4\eta^2 k$, $\alpha = \varepsilon/\sigma$, $\beta = \kappa k/2\eta$, and ε and κ being the surface elasticity and surface viscosity, respectively.

3. Experimental

The experimental setup is shown in **Fig. 1**. The sample is the monomolecular film of ethyl-myristate covering the surface of distilled

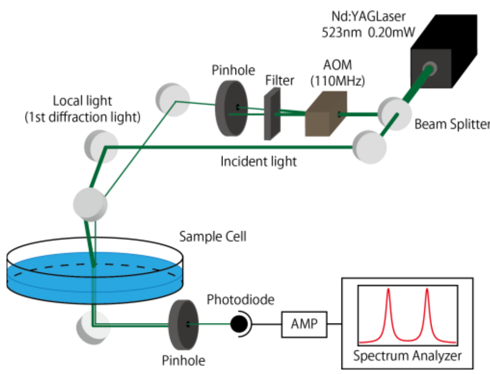

Fig. 1 Schematic view of the ripplon light scattering system.

water. The scattering angle was determined by observing the ripplon propagation on the bare water surface as a reference sample. Then a drop of ethyl-myristate was injected on the water surface. **Figure 2** shows a typical example of the ripplon spectrum obtained at the scattering wavenumber of 1.78×10^{5} m^{-1}.

The experiments were carried out changing the scattering angle and thus the corresponding ripplon frequency in the range of 10 - 300 kHz. All the experiments were conducted at the temperature of 303 K.

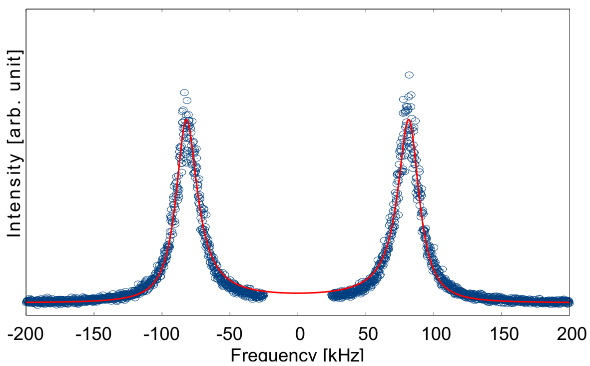

Fig. 2 Typical ripplon spectrum observed for the water surface covered with a mono-molecular film. The solid line shows the theoretical curve derived from eqs (1) and (2).

4. Results and Discussion

Figure 3 shows a chart to relate the ripplon frequency and damping to the surface elasticity and surface viscosity calculated for k=1.78×10^{5} m^{-1}. On the pure water surface, the data is on the origin of the chart represented by an asterisk. The increases in the surface elasticity and viscosity drive the data point toward the tangential and radial direction. The experimental results obtained are also plotted on the chart and they show the surface layer has a finite value of the surface visco-elasticity.

The frequency dependence of the surface visco-elasticity is shown in **Fig.4**, in which we can see the values are almost kept constant. This suggests that the frequency region of the measurement is higher than the relaxation frequency of the monolayer-bulk phase transition. We can also see that $\omega\kappa$ is larger than ε. The surface visco-elasticity is known to be composed of two dependent terms with respect to shear deformation and compression. The most of the viscosity observed here can be, therefore, attributed to the contribution from the shear mode. We are now planning to expand the range of the measurement,

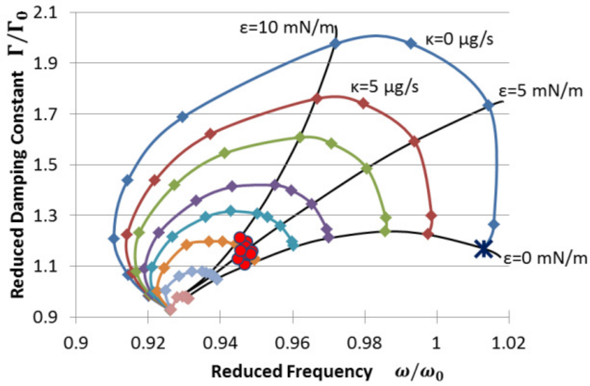

Fig. 3 An example of schematic chart to relate the ripplon frequency and damping to the surface visco-elasticity. The tangential and radial direction represents the increase in the surface elasticity and viscosity, respectively.

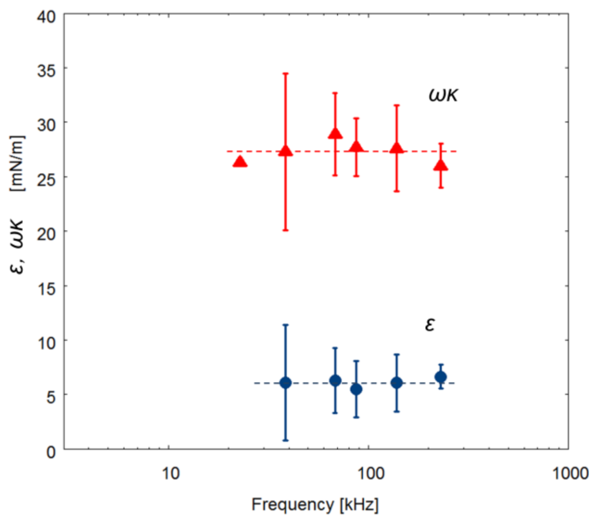

Fig. 4 Frequency dependence of the surface visco-elasticity observed for the mono-molecular layer of ethyl-myristate. The dashed lines are drawn as eye-guides.

especially towards the lower range by employing the ripplon excitation method.

References

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