

Observation of Coexistence of Gas and Condensed Phases in Langmuir Films by Scanning Ripplon Light Scattering Technique

K. Sakai* and K. Takagi

Institute of Industrial Science, University of Tokyo, Roppongi 7, Minato-ku, Tokyo 106, Japan

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Distribution of the mechanical properties of Langmuir films of myristic and stearic acids under the transition from gas to condensed phase was observed by measuring local propagation of thermally excited surface waves (ripplon). Ripplon light scattering system was improved so that the laser beam could be scanned over the surface. Inhomogeneous structure was successfully observed with a spatial resolution of millimeters, in which a stiff film with high surface elasticity and a region with nearly zero surface elasticity coexist and separate into two single domains. The surface elasticity and the area of the stiff phase were qualitatively examined to confirm that the macroscopic droplet observed was a homogeneous liquid film. Fine structure of the boundary between gas and condensed phases was also observed with higher spatial resolution of 100 μm by measuring the propagation of high-frequency ripplon.

Introduction

Langmuir film is known as a two-dimensional material which shows physical behavior analogous to those of bulk material. One of the noticeable phenomena is phase transition occurring in the two-dimensional system. These films take various states such as gas, liquid expanded (LE), liquid condensed (LC), and solid phases depending on the temperature and surface pressure. As for Langmuir films of some typical insoluble carboxyl acids, the transition from gas to condensed phase is known to be the first order and coexistence of the two phases is realized. Observation of the structure formed by the separated phases is of great interest because morphological study on the coexistence structure in Langmuir films would yield valuable information on the phase transition and molecular interaction in the two-dimensional system. Various attempts have been made so far to obtain visual images of Langmuir films as they are on a water surface. In addition to the fluorescence microscopy method, which is one of the most popular techniques these days,¹ ellipsometric microscopy^{2,3} and Brewster angle microscopy⁴ have been applied recently to obtain direct images of Langmuir films. These methods are to detect the difference in the optical properties between coexisting gas and condensed phase. Besides these optical observations, mechanical measurement is also useful to determine the state of the Langmuir films. Miyano observed a local propagation of the capillary wave on the film in the coexistence region and pointed out that the domains of the separated phases have macroscopic structure as large as the order of centimeters.⁵

In this study, we observed the distribution of the mechanical properties in the Langmuir films under coexistence of gas and condensed phases by measuring liquid surface ripplon with a light scattering method and obtained images of separated phases over the whole surface area. Fine structure of the edge of the condensed droplet was also observed with an increased spatial resolution.

Noncontact Characterization of Langmuir Films by Ripplon Light Scattering Measurement

Ripplon is a thermally excited surface tension wave propagating on a liquid surface. The propagation can be observed by a light scattering method with an optical-beating spectroscopy technique.⁶ Measurement is now available up to the frequency of 6 MHz.^{7,8} There have been many light scattering studies of fatty acid monolayers.⁹⁻¹⁴ This technique has various advantages in evaluating the local mechanical properties of Langmuir films. First, it is a complete noncontact and nondestructive method. Only a probe laser beam with the power of 100 mW illuminates the liquid surface giving no significant disturbance thereby. Secondly, we can make mapping of the local structure with spatial resolution as high as several tens of micrometers by focusing the laser beam and observing the propagation of high-frequency ripplon whose wavelength is much smaller than the spot diameter. The greatest advantage lies in the fact that the ripplon propagation feels the viscoelastic nature of the surface as well as the surface tension.¹⁵ The phase transition from gas to condensed phase is known to be of the first order in the Langmuir films of long chain carboxyl acids at room temperature.¹⁶⁻¹⁹ The surface pressure is thus constant and continuous all over the surface area even when both the condensed phase and gas phase coexist on the surface, though line tension along the boundary may possibly bring a very small discontinuity in the surface tension. Con-

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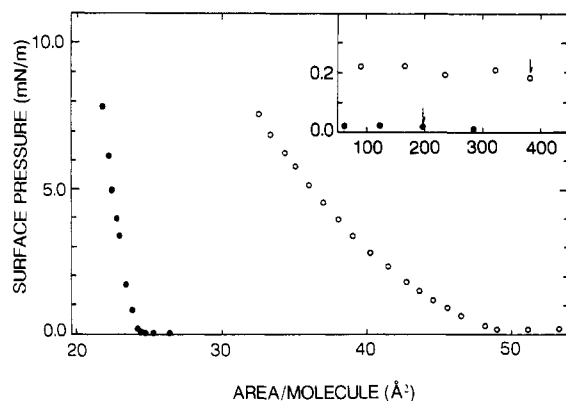


Figure 1. π -A isotherms of myristic acid and stearic acid monolayers represented as open and closed circles, respectively. The inset shows the surface pressure in a dilute region, in which the states of the samples observed are shown by the arrows.

ventional surface tension measurements, therefore, are blind to whether the area under examination is covered with a gas film or a liquid film. The surface elasticity and surface viscosity are, however, quite different between these two phases. Ripplon measurement yields the absolute values of the surface viscosity and elasticity, which give a quantitative measure for characterization of separated phases in a two-dimensional system. In the present experiment, the surface viscoelasticity was actually obtained by nonlinear mean square fitting of the theoretical curve of the power spectrum of the ripplon light scattering to the experimental data.^{6,20,21} Detail of the data analysis has been given in our previous paper.¹⁴ In this experiment, the ripplon light scattering system was improved so that the laser spot could scan over the surface area. The spot size was adjusted from 80 μm to 2 mm with a light collimation system according to the required spatial resolution.

The sample container is a round trough 8.5 cm in diameter and 1 cm in depth and made of glass. Its wall is covered with a thin Teflon sheet, though a trough of other materials was also used as described later. A cover plate of optically flat glass was put on the trough after the monolayer had been expanded. Samples are monomolecular layers of myristic acid [$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$] and stearic acid [$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$] spread on the surface of 0.01 mol/L HCl solution in water. The sample acids were purchased from Merck (>99%) and used without further purification. To check the clean surface of the substrate water, we measured the increase of the surface pressure under surface compression which was applied with a Teflon barrier. The increase was less than 0.1 mN/m while the surface tension of the free substrate was 72.74 mN/m. The pressure-area isotherms of these films were measured and the surface elasticity of the liquid phase was determined from the gradient of the isotherm curve just above the increasing point of the surface pressure. Figure 1 shows the π -A isotherms measured for the present samples. The surface elasticity was about 10 mN/m for the myristic acid monolayer at $A = 48.0 \text{ \AA}^2$, and larger than 30 mN/m for the stearic acid at $A = 24.5 \text{ \AA}^2$. The saturation vapor pressure was 0.20 mN/m for myristic acid film and less than 0.03 mN/m for stearic acid film.

Spatial distribution of the ripplon frequency and damping constant was obtained over the whole surface area at each 3 mm in the orthogonal coordinate on the

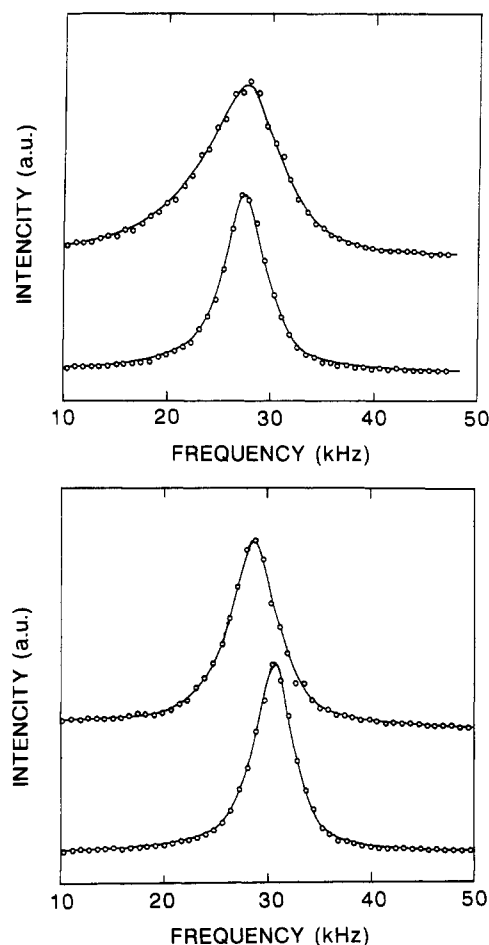


Figure 2. Power spectra of the ripplon propagating on coexisting condensed (upper) and gas (lower) phases observed for (a, top) myristic and (b, bottom) stearic acid monolayers. The solid lines show the theoretical curve fitted to the data.

surface. The wavenumber of the ripplon is determined from the crossing angle of the incident laser beam and the reference beam with an accuracy of 0.1%, which is fixed throughout the scanning. Data acquisition and transfer to a computer took about 10 s for one point and about 1 h to cover the whole surface area. The temperature was kept at 20 °C. Langmuir films were fabricated by dripping *n*-hexane solution of the samples very quietly onto the water surface at the center of the trough. The average areas occupied by a molecule were 385 \AA^2 for myristic acid film and 197 \AA^2 for stearic acid film. The films had been kept for at least 20 min before the light scattering measurements. Surface pressure measured by the Wilhelmy method showed no change from the initial value of the saturation vapor pressure during the addition of the sample solvent, corroborating the fact that the film was under coexistence state.

Figure 2 shows typical power spectra of ripplon light scattering obtained for coexisting gas and condensed phases in (a) a myristic acid monolayer and (b) a stearic acid monolayer. The wavenumber of the ripplon was $7.526 \times 10^4 \text{ m}^{-1}$ in the former and $8.021 \times 10^4 \text{ m}^{-1}$ in the latter. Note that the spectra for the condensed phase are quite different between two samples reflecting the difference in the surface elasticity and surface viscosity. As for the myristic acid monolayer, damping constant of the ripplon is sensitive to the phase difference, while ripplon frequency is a good measure for the stearic acid monolayer. Figure 3a shows a bird's-eye view of the spatial distribution of the ripplon damping on the myristic acid film. A single macroscopic domain which is considered to be the con-

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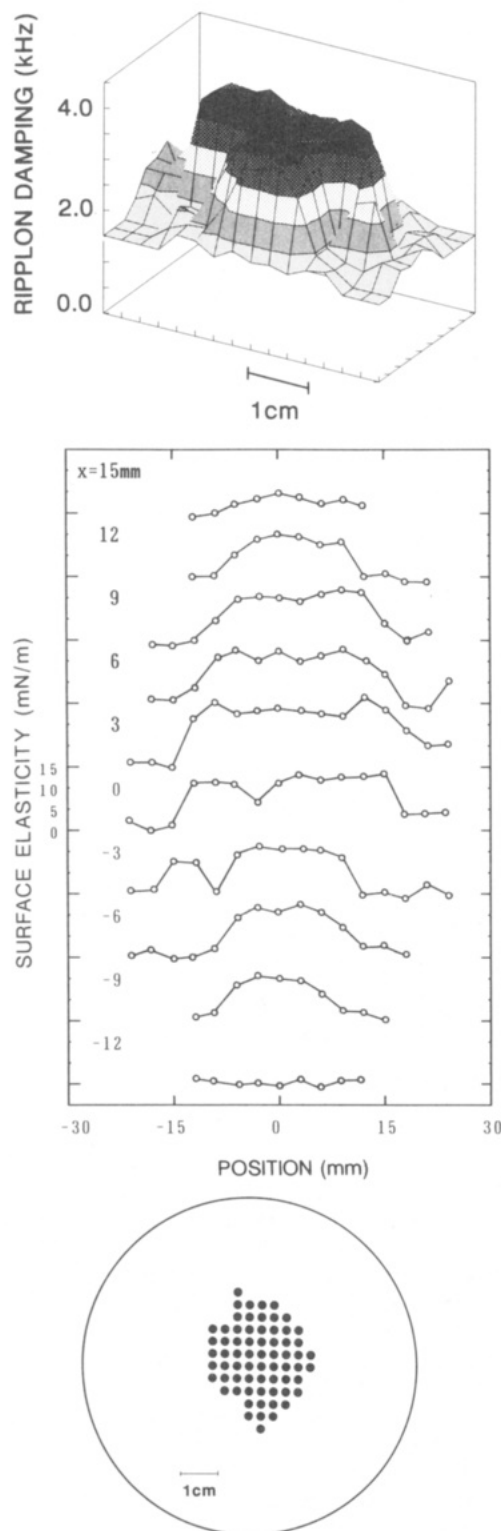


Figure 3. (a, top) Bird's-eye view of the damping constant of ripplon on myristic acid monolayer under liquid-gas coexistence. The wavenumber is $7.526 \times 10^4 \text{ m}^{-1}$. (b, middle) Distribution of the surface elasticity in a myristic acid monolayer. Each curves is shifted by 15 mN/m for clarity. (c, bottom) Shape of the liquid domain on a myristic acid monolayer. Points with surface elasticity larger than 5.0 mN/m are represented by circles. Each circle corresponds to the area actually illuminated by the laser beam.

densified phase is clearly observed. The absolute values of the surface elasticity were determined from the power spectra of ripplon according to Langevin's method²⁰ under assumptions that (i) the surface tension is independent of frequency and (ii) the imaginary part of the surface tension

which is referred to as the surface transverse shear viscosity is negligibly small.¹⁰ The observed spectra were actually fitted well to the theoretical curves derived under the above two assumptions. Figure 3b shows the distribution of the surface elasticity. The surface elasticity of the condensed film is a little higher than 10.0 mN/m, in very good agreement with the value estimated from the π -A isotherms.

Some previous works on dynamic properties of the monolayer films reported discrepancies between the static and dynamic surface elasticity.^{10,13,22} Note that the static surface elasticity given here was obtained by an extrapolation of the π -A curve from the dense side of the end of the condensed-coexistence transition. The surface elasticity of the coexisting condensed film should be same as that obtained from the gradient of the π -A curve just at the dense end of the transition. The surface elasticity of fatty acid monolayer has thoroughly been investigated and believed to decrease rapidly when the condensed film comes close to the end of the transition from the dense side.²³ On the other hand, the surface elasticities by light scattering measurement were, however, almost constant in the region of $\pi < 0.5 \text{ mN/m}$. We consider that the static measurement might be responsible for the discrepancy. Recent studies on pentadecanoic and stearic acid monolayers claimed that such low surface elasticities would be due to the effect of trace impurities included in the sample.^{17,24} Actually, the extrapolation of the π -A curve gives a surface elasticity of comparable order with that obtained by the light scattering measurement. The dynamic measurement might be rather useful to obtain the real surface elasticity at the end of the transition. It is important to know the real surface elasticity from the viewpoint of the study of critical phenomena in the two-dimensional system. Thus we are planning further experiments to examine our hypothesis.

The previous studies also show that films under coexistence have almost the same dynamic surface elasticity as that of condensed phase in the vicinity of the dense end of the transition.^{13,22} These results are quite reasonable because, near the end of the transition, the laser beam most likely illuminates the condensed area which would cover a large part of the surface.

The points whose surface elasticity are larger than 5.0 mN/m are represented by circles in Figure 3c. The condensed phase was found to form a single domain in a circlelike shape around the dripping point. We estimated the area of the liquid phase from the volume of the solution fed onto the surface, taking the portion vaporized to the gas phase into account. The accuracy of the area determination was limited by the spatial resolution (3 mm) and the error was estimated to about 10%. The result obtained for myristic acid is 5.8 cm^2 , which is in very good agreement with the area of the domain (5.8 cm^2) shown in Figure 3c. Here, we did not take the effect of dissolution of surface molecules into account. We should observe the time dependence of the area of the condensed phase in the further study to examine the dissolution effect.

We also determined the surface viscosity and obtained the values $< 5 \times 10^{-9} \text{ N s/m}$ over the whole surface area, without finding any significant difference between the two phases.

The results obtained for a stearic acid monolayer are given in Figure 4, in which (a) shows the spatial distribution

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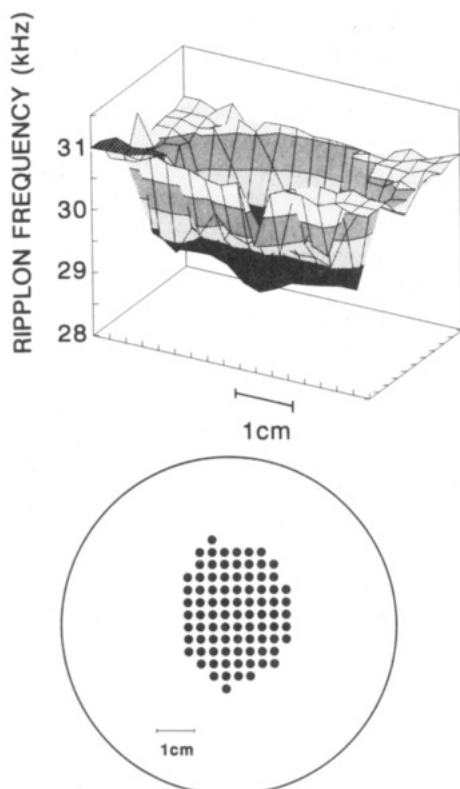


Figure 4. (a, top) Bird's-eye view of the distribution of the ripplon frequency on a stearic acid monolayer under liquid-gas coexistence. The wavenumber is $8.021 \times 10^4 \text{ m}^{-1}$. (b, bottom) Shape of the condensed domain in the stearic acid monolayer. Points with surface elasticity larger than 10.0 mN/m are represented by circles. Each circle corresponds to the area actually illuminated by the laser beam.

of ripplon frequency. Frequency is more suitable than ripplon damping to distinguish a stiff condensed region with surface elasticity larger than 20 mN/m from the soft gas region. The shape of the condensed domain is shown in Figure 4b. The area was estimated to be 7.8 cm^2 , which is in agreement with the expected value of 7.1 cm^2 .

As for the stearic acid monolayer, the ripplon measurement could yield only a rough value, $\epsilon > 30 \text{ mN/m}$, since the ripplon propagation is not sensitive to ϵ when the film has large surface elasticity or surface viscosity, as is the case in stearic acid monolayer. The error in determining the ripplon frequency (1%) and damping constant (5%) lead to more than 100% error of the surface elasticity and surface viscosity when $\epsilon > 100 \text{ mN/m}$. This serious situation can be visually understood from the Hard and Neuman diagram which gives the relation between the ripplon propagation and the surface viscoelasticity.¹⁰

Several works have been made on the state of the gas/condensed phase coexistence in fatty acid monolayers. Their results are, however, not necessarily consistent. Moore et al. applied the fluorescence microscope technique to the stearic acid monolayer¹ and observed gas bubbles floating on the liquid phases at the coexistence concentration of $60 < A < 100 \text{ Å}^2$. The scope of the microscopic observation is as small as millimeters and could not give the information on the macroscopic structure of the monolayer. The results of the surface wave measurements at low frequencies showed, on the other hand, that the gas and condensed phases are separated into large single domains.⁵ The stable and stationary island observed in Figure 3c or Figure 4b seems contrary to the previous works^{12,24} which suggest the domains whose size is ca. centimeters are moving around. The movement might be

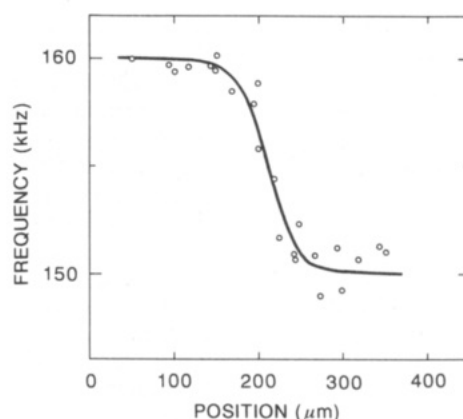


Figure 5. Frequency of the ripplon at the wavenumber of $2.308 \times 10^5 \text{ m}^{-1}$ measured by scanning the laser probe around the phase boundary. The probe beam crossed the phase boundary from gas phase (left) to condensed phase (right). The solid line is drawn as an eye-guide.

caused by convection of the substrate water driven by the temperature gradient. Probably, we could suppress this effect by covering the trough and keeping the temperature homogeneous. Nevertheless, we cannot deny the effect of trace impurities, which may lock the condensed film in the middle of the gas phase. Samples with higher purity would be required to examine the film mobility.

Two important results were derived from the present experiment. The area of the "stiff" part in the film agrees with that of the condensed phase estimated under the assumption that transition from gas to the condensed phase is of the first order and no intermediate phase exists; and the absolute values of the surface elasticity agree well with those obtained from the gradient of the π - A isotherms at the end of the plateau of gas-liquid/solid transition. These facts reasonably lead us to the conclusion that the islands observed are domains of condensed films which do not include a significant amount of gas bubbles. Nevertheless, possibility of the existence of gas bubbles is not denied yet. Actually Figure 3b shows a dip in the distribution of the surface elasticity, which might be a position of a gas bubble. It may also be possible that the condensed domain observed is composed of many microdroplets which have been observed in many coexistence systems by microscopic methods. Unfortunately, the ripplon propagation on inhomogeneous structures, such as porous films and a collection of microdomains, is not clear yet. A theoretical and experimental approach to the ripplon propagation of complex surfaces, as well as higher spatial resolution of the measurement would be required to obtain further information on the microscopic structure.

The curvature of the liquid surface near the trough wall depends on the touching angle of the substrate liquid to it, which can be adjusted by choosing an appropriate material as the wall. We used Teflon as a hydrophobic material and glass as a hydrophilic one, which introduce positive and negative curvature, respectively. The results of the experiment showed that the domain of the liquid phase was stable for both cases and remained in the vicinity of the dripped area at the center of the trough for more than 1 h. Within the scope of the present experiment, we could not find any evidence that the liquid phase suffers from any force induced by the surface curvature.

Observation of Phase Boundary with High Spatial Resolution

We observed the boundary region between the separated gas and liquid phases with spatial resolution increased to

80 μm by collimating the laser beam. The spatial resolution was estimated as the full width of $1/e^2$ intensity of the Gaussian profile of the laser beam, which was measured by the knife edge method. The ripplon wavenumber observed was $2.301 \times 10^5 \text{ m}^{-1}$, which roughly corresponds to the frequency of 150 kHz. Since the decay length of the ripplon is about 240 μm and much larger than the spot size, width of the power spectra is almost the instrumental contribution and yields little information on ripplon damping. Therefore only the peak frequency was measured. Figure 5 shows the ripplon frequency plotted against the position of the scattering area obtained around the phase boundary between gas and condensed phases in a stearic acid monolayer. The frequency decreases as the spot crosses the boundary from gas side (left) to liquid phase (right). The transition occurs within the thickness of 100 μm , which is comparable to the laser spot diameter. The boundary was thus found sharp within the spatial resolution of this experiment.

Conclusion

Local mechanical properties of the Langmuir films on water surface in the coexistence region were investigated

with the ripplon light scattering experiment. We found a macroscopic domain of condensed phase surrounded by a gas region, whose shape and position were stable for an hour. While the present experiment provides us with a very good method to observe a macroscopic structure of the surface, its spatial resolution is still insufficient to see the microstructure. The complementary use of the present technique and the previous surface microscopy technique would make a powerful tool for the investigation of the surface structure.

We are now investigating the effect of film compression or expansion process on the structure, as well as the collision process of liquid phases. For these purposes, a rapid measurement technique to see transient phenomena is required, which would be realized by high-speed beam scanning as well as rapid data processing. Morphological study of Langmuir films would give important information to understand physics of two-dimensional material.

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