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Phase transition and critical behavior in Langmuir films of myristic acid

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A ripplon spectroscopic study was performed on a myristic acid monolayer under the coexistence state of the two-dimensional liquid and vapor phases spread on a water surface. The surface elasticity was observed over the temperature range from 20 °C to 60 °C in both the liquid and the gas regions. The former showed a monotonic decrease with temperature from 1.2×10^{-2} to 2×10^{-3} N m^{-1}. The van der Waals equation of state was assumed to describe the present two-dimensional system after an appropriate modification and the Π-A isotherms were theoretically calculated so that the surface elasticity predicted from these curves agrees well with the observed values. The two parameters characterizing the equation were determined: $a=6.5\times10^{-39}$ N m^3 and $b=3.9\times10^{-19}$ m^2, which are associated with effect of the attractive force and the excluded area, respectively. These values gave the critical temperature $T_C=85$ °C. The validity of the elasticity measurement for studying the two-dimensional critical behavior was discussed. [S1063-651X(96)06306-4]

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INTRODUCTION

It is widely known that many types of amphiphilic molecules form insoluble monomolecular films on water, which are often called Langmuir films. Each molecule turns up its hydrophobic tail into air with the hydrophilic head down in water. Since they are confined to the air-water interface and allowed to move only within the plane, they make an ideal two-dimensional system. Langmuir films take various states, depending on temperature and density, in a manner similar to the phase transition occurring in the usual three-dimensional fluids. Though the Langmuir films are often involved in more complicated phase transitions than three-dimensional fluids, its most dilute phase approximately follows the simple equation of state for an ideal gas. Studies on the nature of the transition between this gas phase and the neighboring condensed phase have been undertaken and the transition has been verified to be of first order in some films. Some fatty acid films, for instance, undergo this sort of transition, which is called a liquid expanded to gas transition [1–5].

The phase transition and its critical phenomena have attracted considerable notice since they give various information on the interaction of particles. The experimental study on the two-dimensional fluids is still in its early stages, presumably because of the technical difficulty, and the comparison between the experiment and appropriate theorem has not yet been sufficiently done. Nevertheless, very intensive studies have been made on the surface pressure Π vs area per molecule A and the two-dimensional critical phenomena have been discussed. Hawkins and Benedek [1] measured nine Π-A isotherms of pentadecanoic acid monomolecular film changing its temperature and obtained the critical temperature for the condensed-gas transition at 26.9 °C. They also discussed the related order parameters and explained their behavior within the framework of mean-field theory. Kim and Cannell [2] also investigated the same material and obtained $T_C=26.27$ °C, in good agreement with the above value. However, the temperature dependence of the order parameters they observed was inconsistent with the former. Pallas and Pethica [5] also studied pentadecanoic acid monomolecular film and obtained isotherms much different in shape from those of the above two groups. They suggested that the critical temperature was over 50 °C. Thus the previous studies are not necessarily consistent with each other, leaving some points open to question.

While the Π-A measurements are static studies of the monomolecular films, the light scattering study of thermal ripplon gives a dynamic approach to the films, in which the phenomenon can be discussed in terms of the viscoelastic property of the two-dimensional materials. In our previous studies [6], we developed a ripplon light scattering technique useful over a very wide wave-number range from 4×10^4 to 3×10^6 m^{-1}.

We have used this technique to study a myristic acid film in its coexistence system of liquid and gas [7]. We scanned the probe laser over the surface area and found that the liquid phase assembles and forms a single macroscopic domain. The simultaneous existence of liquid and gas is manifest evidence of a first-order transition. Such a phase separation of gas and liquid phase is reported by Winch and Earnshaw [8]. They observed the temporal fluctuation of the ripplon spectrum for a pentadecanoic acid monolayer and attributed it to drift of a liquid domain in the coexistence gas. Similar results were obtained by Kim and Cannell [9] in the measurements of a local surface potential.

The condensed film, which has surface elasticity much larger than the gas phase, was readily detected by the light scattering experiment and the shape of the domain was observed in the scanning of the laser spot over the surface. Note that one cannot distinguish between the two phases by the conventional Wilhelmy method since the equilibrium condition requires a uniform surface energy throughout the surface. The trivial effect of the line tension around the domain is safely neglected.

In this paper we describe the critical behavior of the monomolecular films of myristic acid, which is expected to show a phase transition similar to the pentadecanoic acid film. We made the ripplon light scattering experiment to measure the temperature dependence of the surface elasticity

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under the coexistence state below the expected critical temperature.

EXPERIMENT

The difference in the surface elasticity between the phases sometimes gives great contrast to the observed ripplon damping. As for ripplons propagating on the myristic acid monolayer, for example, the decay length in the condensed phase is typically one-third of the value in the gas phase, which has almost the same value as the bare surface of water. This is the reason why we decided to make the ripplon measurement for the present purpose.

Details of the ripplon light scattering experiment have already been given elsewhere [6], so we offer a brief account here. Coherent light of an Ar ion laser is incident on the liquid surface and scattered by thermally excited ripplons into the angle of diffraction determined with the ripplon wavelength. The light frequency shifts and broadens through the scattering process, reflecting the ripplon frequency and a finite lifetime, which are obtained from the power spectrum of the scattered light observed with the optical beating spectroscopy technique. The shape of the spectrum is given by a very complicated equation, which includes parameters of the surface mechanical property [10] as

$$S(k,\omega)=\frac{k_BT\rho}{4\pi\omega\eta^2k}\,\mathrm{Im}\left[\frac{\omega^2-\varepsilon^*k^3(m-1)/\rho}{D(\omega)}\right],$$

where

$$D(\omega)=\omega^2\left\{\frac{1}{4}\,(m^2+1)^2+\frac{\gamma\rho}{4\eta k^2}-m\right\}+\frac{\rho\varepsilon^*}{4\eta^2k}\left\{\omega^2m+\frac{\gamma}{\rho}\,k^3(m-1)\right\}$$

and

$$m=\left(1-i\,\frac{\omega\rho}{2\eta k^2}\right)^{1/2},\quad \varepsilon^*=\varepsilon-i\omega\kappa,\quad \gamma=\gamma_0-\Pi. \qquad (1)$$

Here ω is the angular frequency, k is the ripplon wave number, ε^* is the complex surface elasticity, ε and κ are the surface elasticity and surface viscosity, respectively, and η and ρ are the bulk shear viscosity and the density of substrate water, respectively. The surface pressure Π is given by the Wilhelmy method as the difference between the surface tensions of the bare water surface γ_0 and that of the membrane γ as $\Pi=\gamma_0-\gamma$. In this study, the scattering angle was fixed at $\theta=0.4°$, which gives $k=9.5\times10^4\ \mathrm{m}^{-1}$. The power spectrum has two peaks that are symmetric with respect to the central frequency, and the peak frequency and the width of each component roughly correspond to the ripplon frequency and temporal damping constant, respectively. A rigorous analysis of this equation to determine the surface elasticity from the observed spectrum would imply an enormous and somewhat pessimistic effort. Instead, we took a more practical way to obtain ε^* from the observed peak frequency and the width. We calculated a series of theoretical curves with different values of ε and κ and determined the peak angular frequency ω_P and the half-width $\Gamma/2\pi$ of each spectrum. Thus one set of ω_P and Γ gives one set of ε and κ in a one-to-one correspondence, as shown in Fig. 1. We prepared a series of such diagrams for different temperatures. This way of analysis enables us to treat the numerous data simply and rapidly. The data were accumulated and averaged for about 3 min to improve the signal-to-noise ratio.

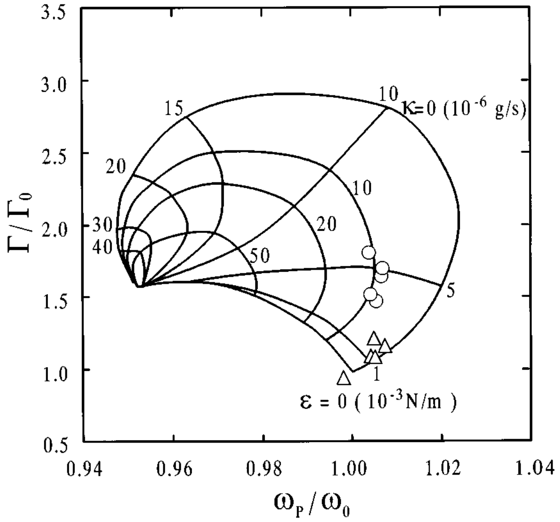

FIG. 1. Diagram on which the complex surface elasticity is determined. One ripplon spectrum gives a point (ω_P,Γ), which corresponds to a set of ε and κ on this chart. Both coordinates are normalized with respect to ω_0 and Γ_0, values of ω_P and Γ for clean water surfaces. The elasticity ε increases counterclockwise along semicircles, of which the outermost one is for $\kappa=0$. The semicircle shrinks as κ increases. The circles and the triangles indicate the results of the liquid and the vapor phase, respectively. This chart is for $T=47$ °C.

The sample container is a round trough made of glass 10 cm in diameter and 1 cm in depth. The container was repeatedly rinsed by distilled water to get a clean substrate of water and was put in a thermostatic box. The temperature of the sample is kept constant throughout the light scattering experiment within an accuracy of ±0.5 K. The laser light passes downward through the optical windows at the top and the bottom of the thermostatic box.

The key technique of this experiment is how to make a large domain of the condensed phase in required area. The sample film is prepared as follows. A Teflon sheet of 50 μm in thickness is cut into the shape shown in Fig. 2 and floated on the surface of 0.01 mol L of HCl. The surface is divided into the central circle and the outer area, which are interconnected through a narrow channel 1 mm in width. Myristic acid solved in n-hexane is added on the surface of the inside area. A highly condensed phase is formed therein. Then the vapor of the myristic acid goes through the channel to the outside area and fills it at the saturated vapor pressure. The more viscous condensed phase would be reluctant to go through the narrow channel, which works as a two-dimensional capillary tube. Adding an appropriate amount of the solution, we can perfectly fill the inside area with the condensed phase, while almost all of the outside is occupied by the gas phase. We confirmed this situation of phase separation between these two areas actually by the light scattering experiment made at some sampling points on each area.

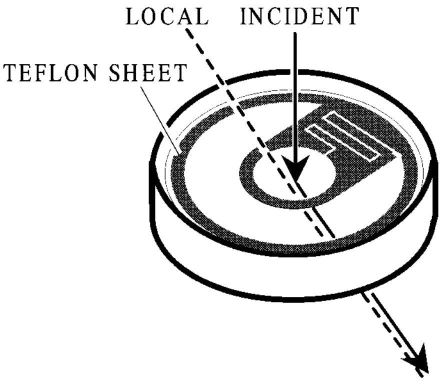

FIG. 2. Surface of observation. The Teflon sheet loosely divides the surface into two areas. The specimen is dripped onto the inner circle, where a liquid phase is expected. The coexistence gas is likely to go through the narrow channel to the outer ring. The light scattering is made at a certain point on both areas. The solid arrow is the incident light while the dashed is the reference of the optical heterodyne.

The measurement was carried out only when the following two conditions were satisfied. (i) The ripplon spectra observed are obviously different between the inside and outside areas and the inside area has a higher surface elasticity. This condition corroborates the fact that the monolayer is under the coexistence state with the condensed phase inside and the vapor outside. At high temperatures, the difference in ε between the two phases is smaller than the experimental error of 2×10^{-3} N m^{-1} and we cannot clearly distinguish between them. (ii) The power spectra for the both areas are stable and the surface elasticity is kept at a constant value within 1.5×10^{-3} N m^{-1} for more than 10 min. At high temperatures, we sometimes experience that the ripplon spectrum characteristic to the liquid phase gradually changes to that of the gas. It is possibly because the vaporization occurred in the domain of the condensed phase and the gas bubble grew there. These phenomena might occur due to a slight temperature inhomogeneity. Figure 3 shows the behavior of the surface elasticity of the ‘‘stable’’ and ‘‘unstable’’ liquid phases. A monomolecular film of myristic acid generally reaches a stable state a few minutes after the film expansion and the liquid phase stably exists for more than 10 min, as shown in Fig. 3(a). In Fig. 3(b), however, the surface elasticity continues to decrease to zero. The probing laser happened to have illuminated the vaporized area in the condensed phase. In these cases, the data were eliminated and a new sample was prepared. A similar phenomenon was reported to happen in pentadecanoic acid monomolecular film [8]. Myristic acid was purchased from Merck and used without further purification.

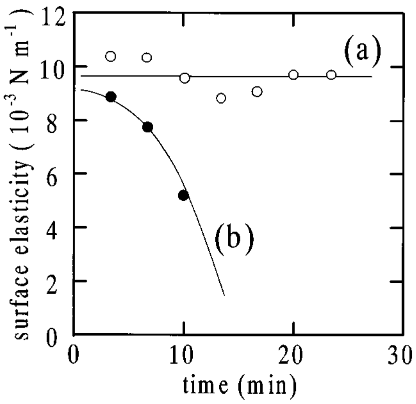

FIG. 3. Two typical behaviors of surface elasticity, of which (a) shows a stable existence of the liquid phase while (b) otherwise.

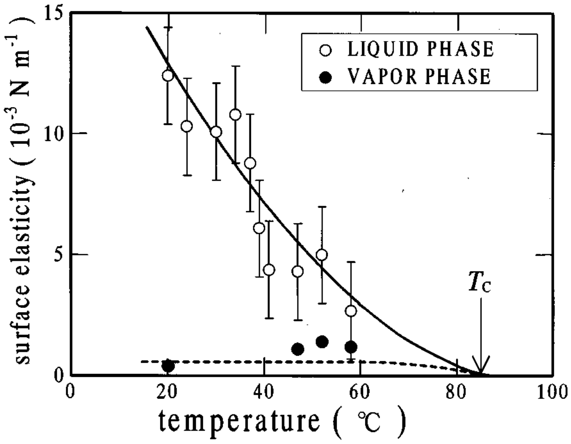

FIG. 4. Surface elasticity ε_l (open circles) and ε_v (closed circles) observed at different temperatures. The solid line represents a theoretical curve fitted with the aid of van der Waals equation in the manner given in the text. The dashed line is the theoretical curve for ε_v calculated on the Π-A isotherms determined in the fitting.

SURFACE ELASTICITY AND CRITICAL POINT

The surface elasticity was observed in both phases, ε_l for liquid phase and ε_v for vapor phase, over the temperature range from 20 °C to 60 °C. The results are shown in Fig. 4, where the open and closed circles represent ε_l and ε_v, respectively. While ε_v shows no appreciable difference from the values on a clean water surface, the liquid phase has a substantial elasticity that decreases monotonical with temperature and approaches ε_v. Does this temperature dependence imply that the coexistence system is going toward the critical point or does it simply reflect the normal softening of a heated elastic film?

Generally speaking, the critical point of the two-dimensional substance should be treated and discussed on the basis of Π-A curves. The static study of the isotherms gives the dense and dilute ends of the coexistence region at $A=A_l$ and A_v, respectively. The locus of these points obtained at many different temperatures defines the binodal, of which the maximum gives the critical point. No doubt, this would be the most direct approach to the phenomenon. The fact is, however, that the accurate and reliable determination of A_l and A_v is very difficult. There are some cases in which the surface pressure observed in the coexistence region near A_l shows a slight and gradual increase toward the liquid side. The absence of a sharp edge would result in an uncertainty in A_l and ε_l as the gradient of the curve at $A=A_l$, as has been discussed by Pallas and Pethica [5]. The previous studies are not necessarily in harmony and, in some aspects, seem to contradict each other.

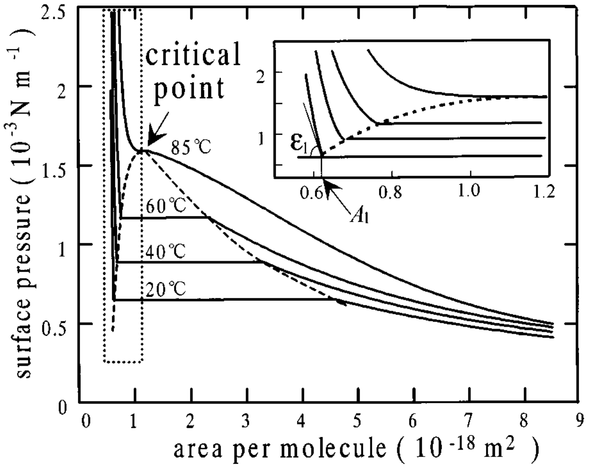

FIG. 5. Examples of Π-*A* isotherms theoretically given by the van der Waals equation of state. These curves were calculated with those parameters of *a* and *b* determined in the fitting of Fig. 4. The narrow square region indicated by the dotted line is expanded and shown in the inset. The curve at 20 °C gives $A_1 = 6.2\times10^{-19}$ m^2, which is in reasonable agreement with the value 4.8×10^{-19} m^2 obtained in the static Π-*A* measurement. The elasticity ε_l appears in this diagram as the differential at $A = A_l$. The solid line of Fig. 4 is fitted so that it agrees with the experimental value of ε_l obtained at each temperature in the ripplon measurement.

The above scheme of a Π-*A* analysis is a simple analogy of the classical way to describe the gas-liquid transition in three-dimensional substances. The shape of the *P*-*V* isotherms is given by the famous van der Waals equation of state based on the mean-field theory. Hawkins and Benedek [1] used this equation successfully in the two-dimensional system and explained their experimental results on pentadecanoic acid film. After an appropriate reduction of dimension, the van der Waals equation of state is written as

$$\Pi = \frac{k_B T}{A-b} - \frac{a}{A^2}, \tag{2}$$

where k_B is the Boltzmann constant and *a* and *b* are the parameters characteristic to the molecule. Given *a* and *b*, we can draw the whole shape of Π-*A* isotherms at any temperature, as illustrated in Fig. 5. The surface pressure at the coexistence region Π_S is determined by the Maxwell construction principle. The surface elasticities obtained by the ripplon spectroscopy appear in this diagram as the gradient of the curves:

$$\varepsilon_l = -A_l \left(\frac{d\Pi}{dA} \right)_{A_l}, \quad \varepsilon_v = -A_v \left(\frac{d\Pi}{dA} \right)_{A_v}. \tag{3}$$

Both ε_l and ε_v decrease to zero as the system is heated up to T_C, the critical temperature. The van der Waals equation of state, when *A* is large enough, reduces to the well-known simple equation of state for ideal gas, $\Pi = (k_B T)/A$.

It should be emphasized again that we carried out the experiment, always keeping in mind to ascertain the coexistence state. We were precisely at A_l and A_v, though their values are unknown, and traced the binodal line to T_C.

We actually obtained *a* and *b* so that the calculated values of $-A_l(d\Pi/dA)_{A_l}$ and their dependence on temperature agree well with the experimental points of Fig. 4. The solid line in the figure represents the theoretical curve thus determined. In spite of the very tight curve fitting with only two adjustable parameters, the agreement is fairly good. The obtained parameters are $a = 6.5\times10^{-39}$ N m^3 and $b = 3.9\times10^{-19}$ m^2. Nevertheless, we should be very careful about this result, which apparently supports the hypothesis that the van der Waals equation of state can describe the two-dimensional system. First, the validity of *b* is checked. This parameter represents the effect of the excluded area and is to be compared with the vertical projection of the molecule standing upside down. The above value of *b* gives quite a reasonable diameter, 7 Å. The other parameter *a* is associated with the attractive force. Though this parameter cannot be examined in the absence of any appropriate value to be compared with, the Π-*A* isotherms determined by Eq. (2) with these values of *a* and *b* are consistent with the observed curves, except that Π_S shows considerable disagreement in some cases. This problem of Π_S is discussed in the following section. Finally, ε_v was determined from the gradient of these curves and shown by the dashed line in Fig. 4, which is in good agreement with the experimental points. Thus the present trial of getting the critical point by manipulating the van der Waals equation seems to be an appreciable success. The critical point was determined as $T_C = 8a/27k_B b = 85$ °C, $\Pi_C = a/27b^2 = 1.6\times10^{-3}$ N m^{-1}, and $A_C = 3b = 1.17\times10^{-18}$ m^2.

Since the van der Waals equation of state is based on the mean-field theory, the above successful curve fitting suggests the mean-field behavior of the molecules. In the previous studies on pentadecanoic acid films, an intensive consideration on the critical exponents also indicated that the transition is acting mean-field-like, not Ising-like [1,2].

DISCUSSION

The first criterion of liquid or gas is in the state of concentration, dense or dilute. The study of Π-*A* isotherms is surely from this standpoint and the experiment directly gives A_l and A_v. The present study of ripplon spectroscopy proposes another criterion, which recognizes liquid or gas by the elasticity, hard or soft. The differentials at A_l and A_v also characterize the system. The curve being almost upright at A_l in the coexisting liquid lays itself as *T* approaches T_C. This edge at A_l would be a vital point of the curve: The whole shape is sensitive to the gradient at the point. This is why ε_l as a function of *T* can predict T_C with the aid of the van der Waals equation of state.

As stated in the preceding section, Π_S obtained by the van der Waals equation was sometimes inconsistent with the values observed by the Wilhelmy method [7] and the difference can be a factor of 3–4. The present method was shown to be very poor at yielding Π_S. The reason is obvious in Fig. 5. At temperatures of this experiment, the Π-*A* curve is very steep and almost straight in the liquid region near A_l. Hence a substantial change in Π_S gives but a trivial difference in ε_l. Conversely speaking, ε_l is hardly sensitive to Π_S. However, this fact poses no serious problem in the present study. On the contrary, here is the advantage of the ripplon experiment, which gives ε_l under the coexistence state.

The measurement of the surface pressure is intrinsically difficult and delicate since it must be done under the strongly biased field of surface tension. The value directly measured by the Wilhelmy method is not Π but the surface tension, whose decrease in the presence of monolayer film is recognized as Π. The decrease is, however, less than 2% of the surface tension. A negligible error in the surface tension is greatly magnified and would give a serious error to Π. This fact can be one of the causes of the disagreement between the previous results of Π-A studies, though very careful and fine experiments have been done.

Measurement of ε_l by the ripplon light scattering depends very weakly on Π, on the other hand, and a very rough value of Π including more than 50% error is enough. The surface tension mostly determines the ripplon propagation as its restoring force and Π affects the wave only through a very slight decrease of less than 2% in the surface tension. The surface elasticity is not subject to Π, the most delicate value. But this is quite natural: The dependence of elasticity on pressure means higher-order elasticity, and the third-order effect in normal liquids is very small, the change in elastic constant being 10^{-4} in 1 atm.

In conclusion, the present study proposes another approach to the critical behavior in the two-dimensional gas-liquid system. The ripplon measurement made in the liquid phase under coexistence gives the surface elasticity, which guides us toward the critical point exactly along the binodal line. While it has advantages, including the independence on surface pressure measurement, there is a negative aspect to be noted. One cannot arrive at nor go into the vicinity of the critical point, though the van der Waals equation can derive it theoretically. The experiment should be made in the distinct coexistence state, which can be confirmed at least 20 °C below T_C. Nevertheless, the dynamic approach proposed here would be important as a complement to the more direct way of Π-A study.

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