## Experimental study of a two-dimensional gas-liquid phase transition\*

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The surface pressure exerted by a monomolecular layer of pentadecanoic acid spread on a pH-2 distilled-water substrate has been measured as a function of temperature and surface density in the vicinity of the gas-liquid critical point for this two-dimensional system. From these measurements, the shape of the gas-liquid coexistence curve and the isothermal compressibility along both sides of the coexistence curve and above the critical temperature are deduced. In agreement with the findings of Hawkins and Benedek obtained on pure distilled water, we find that a true phase transition exists between the liquid and gaseous states of the film and that the behavior of the film in the vicinity of its critical point can be characterized by power-law behavior with mean-field exponents. We do not, however, find it possible to interpret all of our data in terms of a simple mean-field phase transition.

#### I. INTRODUCTION

The possibility of forming a monomolecular layer of an insoluble substance on the surface of water was first discussed scientifically in 1774.<sup>1</sup> It was not until the early twentieth century, however, that quantitative studies of the properties of such films were undertaken.<sup>2</sup> Measurement of the surface pressure as a function of available area per film molecule soon provided evidence for a variety of phases for these systems.<sup>3</sup> In 1926 Adam and Jessop<sup>4</sup> established that in the limit of a large available area per molecule such films behave as two-dimensional ideal gases, but that as a film is compressed it departs from ideal behavior and condenses into a liquid state. They also noted that films formed of sufficiently lowmass molecules did not condense at the temperature used in their experiments, and they surmised that surface films would exhibit a gas-liquid coexistence curve if studied at a variety of temperatures.

Hawkins and Benedek<sup>5</sup> have recently measured such a coexistence curve for a film of pentadecanoic acid,  $CH_3(CH_2)_{13}COOH$ , spread on a pure distilledwater substrate, and found it to exhibit meanfield behavior. We have been independently engaged in making similar measurements for several years using the same substance on a pH-2 distilled-water substrate and have obtained results which differ from theirs in several respects. Our results do confirm their findings that the system has a true coexistence curve and that the isothermal compressibility along the liquid side of the coexistence curve,  $(\kappa_T)_i$ , varies as  $(\rho_i - \rho_v)^{-2}$ , where  $\rho_i$  and  $\rho_v$  are the densities in molecules/10<sup>4</sup>  ${
m \AA}^2$  along the liquid and vapor sides of the coexistence curve, respectively. For the liquid phase

we find

 $(\kappa_T)_I \propto (\rho_I - \rho_v)^{-2 \cdot 01 \pm 0 \cdot 13}$ 

and for the vapor

 $(\kappa_T)_v \propto (\rho_I - \rho_v)^{-1.94 \pm 0.11}.$ 

However, for a given value of  $\rho_1 - \rho_v$ , our values of  $(\kappa_T)_1$  are as much as 20 times larger than theirs, and the actual measured surface pressures differ by as much as a factor of 2. We also find different values for the critical pressure and density. Our measurements also reveal that the compressibility above the critical point is *less* than that of either coexisting phase for any given temperature difference from the critical temperature  $T_c$ , in conflict with the results of mean-field theory. A brief summary of the pertinent results of this work has already appeared.<sup>6</sup>

## **II. EXPERIMENTAL METHOD**

Figure 1 is a schematic diagram of the apparatus used to measure the film pressure. The inside dimensions of the substrate trough are  $47 \times 18$  $\times 0.64$  cm. It was milled from a single piece of Teflon fastened to an aluminum base plate by screws. The milling cutter was cleaned in trichloroethylene before use, and the milling was carried out using a large piece of construction paper to protect the trough from accidental contamination by oil from the milling machine. Before attempting to use the trough it was cleaned in acetone, rinsed in hot running tap water for several hours, and rinsed repeatedly in distilled water.

In use, the trough was filled to a height of ~3 mm above its top surface, and the water surface was cleaned by repeatedly sweeping it using two  $21 \times 1.27 \times 0.95$ -cm Teflon bars in tandem on each





side. The sweeping bars were pinned into slots in stainless steel holders to keep them accurately flat. The bars were cleaned between sweeps by flushing them with reagent-grade acetone and rinsing immediately afterward in distilled water. Surface contaminants trapped between the bars and the ends of the trough were removed periodically by suction using an aspirator and a 20-gauge hypodermic needle. This necessitated the occasional addition of water to the trough during the cleaning process.

The problem of sufficiently cleaning the trough and all apparatus in contact with the water is a very substantial one. The rate at which surface pressure builds up because of contamination must be low enough for the contamination which accumulates in several hours to have a negligible effect on the measurements. No method of cleaning the trough prior to filling it with water seemed even remotely adequate.

The system eventually reached a state of clean liness where the pressure due to contamination increased at the rate of 2 mdyn/cmh, and was identical on both sides of the trough. This was achieved by keeping the trough filled with warm, triply distilled water and sweeping the surface every few hours during the day for a period of six months. The water was changed twice a day throughout this period. Once cleaned in this manner, the pressure arising from contaminants could be reduced to less than 4 mdyn/cm on both sides of the surface-pressure measuring thread by less than 1 h of sweeping. The pressure quoted was actually measured  $\frac{1}{2}$  h after sweeping, this being the time required for the water itself to reach thermal equilibrium after the sweeping process. All data were taken on surfaces prepared in this manner, with initial contamination pressures of less than 10 mdyn/cm, and the results were independent of the exact degree of contamination in this regime. Further evidence to the effect that the contaminant molecules did not interact with the pentadecanoic acid film will be presented below.

In the course of cleaning the apparatus, many possible causes for the contamination were suspected and eliminated as possibilities. Among these were the air above the trough, the water itself, glass and metal materials in or near the trough, and the paraffin used to coat objects in contact with the water. We feel that by far the most likely source of contamination in our case was from the Teflon itself.

The surface pressure was measured using a technique invented by Guastalla.<sup>7</sup> In this method the water surface is separated into two regions by means of a very light silk thread which forms a barrier that is impenetrable to a monolayer. The measuring section of the thread was maintained under tension by a needle and torsion wire as shown in Fig. 1. The torsion wire was a 0.03cm-diam stainless-steel wire 72.8 cm long, and the needle, which was also stainless steel, was 10 cm long. The measuring thread was made by drawing two pieces of  $20 - \mu m$ -diam surgical silk thread through molten commercial paraffin to make them water repellent. They were then fused along most of their lengths by drawing them together across a hot stainless-steel rod. At the end where the individual threads had not been joined, one end was attached to the bottom of a 0.5-cm-diam mica disk using Duco Cement. The disk had a 0.1-cm-diam hole in its center through which the tensioning needle passed. The disk and cement were covered with a thin layer of paraffin by dipping them in molten paraffin.

The ends of the measuring thread were joined to the edges of the trough by sandwiching them between two pieces of microscope slide  $1.8 \times 0.2 \times 0.3$ cm which were then glued together with paraffin. The edge of the lower slide was not coated in the vicinity of the thread. This enabled the water to wet the clean glass and come into contact with the thread, forming a leak-free joint. The assembled thread was positioned by gluing the pieces of microscope slide to the trough with paraffin. Some skill is required to fabricate these joints, but once functioning they usually last for several weeks.

The presence of an excess of surfactant molecules on one side of the thread caused it to sag away from them, forming a segment of a circle. The sag S as defined in Fig. 1 was measured by using a 3.6-cm-focal-length lens to image the thread on a screen 3.6 m from the trough. The thread was illuminated from below using a small mirror to reflect light upward from the bottom of the trough. The sag could be measured with a precision of  $\pm 2 \times 10^{-4}$  cm in this way. The force per unit length,  $\Pi$ , exerted on the thread by the molecules is related to the tension *T* and the sag by

$$\Pi = 8TS / (L^2 - 4S^2),$$

where the length L is as shown in Fig. 1. The shorter section of the thread was chosen to have a length such that it formed a semicircle under the influence of the film pressure and thus did not alter the tension applied to the measuring section of the thread by the needle by any appreciable amount.

The spring constant of the torsion wire was measured by replacing the needle by two weights and measuring the period of torsional oscillations. The wire could be rotated at one end to change the tension. Since the tension depends on the angular position of the needle as well, this was measured by reflecting a cross-hair pattern in a light beam from a small mirror glued to the joint of the needle and the torsion wire. The over-all accuracy of pressure measurement was ~1%. Changes in the film pressure as small as 0.02 mdyn/cm could be detected when the pressure difference across the thread was less than 2 mdyn/cm.

When making measurements in the vicinity of the coexistence curve, a film consisting partially of gas and partially of liquid phase was spread on one side of the thread and the film to be studied was spread on the other. This enabled us to study with great precision the very flat portions of the isotherms in the vicinity of the coexistence curve. It would be exceedingly difficult to determine which portion of the isotherms are actually horizontal without using this method. In studying the isotherms above the critical temperature, film was again spread on both sides of the thread, but no horizontal portions could be detected.

Since the surface tension of pure water varies with temperature at the rate<sup>8</sup> of  $\sim 150$  mdyn/cm K, it is necessary for the surface temperatures on both sides of the thread to be maintained equal with great accuracy. This was achieved by enclosing the entire apparatus in a double-walled aluminum box through which temperature-controlled water was circulated. The air above the water was kept saturated with water vapor to prevent surface cooling by evaporation. The water temperature was measured by using a glass-encased thermistor in contact with the surface. It was not coated with paraffin, so that the water would wet it. During the course of measuring one isotherm the temperature was constant to within ±0.003 K, but the changes were very gradual and apparently occurred simultaneously on both sides of the thread.

Water to be used as the substrate was prepared

by triple distillation in interconnected glass stills. The second distillation was carried out over  $KMnO_4$  to remove organic contaminants from the water. The water was conducted directly to the trough from the bottom of a glass storage tank fed by the third still. We did experience some difficulty in attempting to use water which was distilled after being deionized by means of an ion exchange column, presumably because of contamination by slightly volatile impurities from the exchange column. Fresh water was used for each isotherm measured.

Pentadecanoic acid [(95-99)% purity] obtained from K and K Laboratories was purified by recrystallization from petroleum ether. The recrystallization process was carried out twice. Before purification the isotherms contained no truly horizontal portions, the difference between the liquidphase and gas-phase pressures being ~4mdyn/cm at 20 °C. The fact that this effect did not occur when using purified pentadecanoic acid indicates that the residual contamination left on the water surface after sweeping interacted with the film very weakly if at all. The film to be studied was spread by dissolving the pentadecanoic acid in reagent-grade petroleum ether and applying this solution 5  $\mu$ l at a time to the water surface using a micropipet. After spreading a film, approximately 2 min was required for equilibrium to be reached, presumably because of surface cooling caused by the solvent evaporation.

We did not attempt to measure isotherms by compressing a single film since this would have resulted in the compression of any contaminants as well. Since the pentadecanoic acid is a weak acid, it must be prevented from dissociating and reacting with any impurities such as metallic ions present in the substrate. We used pure HCl to adjust the substrate pH to 2 to prevent this effect. When this was not done the film pressures were found to change with time and to vary depending on whether the substrate had been freshly distilled or had been stored for a day or more.

# **III. RESULTS AND DISCUSSION**

Using the apparatus and methods described in Sec. II, we have measured the surface pressure exerted by a monomolecular layer of pentadecanoic acid in the temperature range 14.8–34.7 °C for film densities ranging from  $\rho = 2$  to 200 molecules/  $10^4 \text{ Å}^2$ . The results of these measurements, together with those of Hawkins and Benedek<sup>5</sup> and the single isotherm taken by Adam and Jessop<sup>4</sup> are shown in Fig. 2. Our results are in fairly good agreement with the one isotherm of Adam and Jessop, who also used a pH-2 substrate, but dif-



FIG. 2. Surface pressure vs density for a film of pentadecanoic acid spread on a pH-2 water substrate. The isotherms are labeled in °C and a few representative data points are shown. The dashed curves show the results of Hawkins and Benedek obtained on distilled water alone; the single isotherm taken on a pH-2 substrate by Adam and Jessop is shown as a dotted line.

fer from those of Hawkins and Benedek quite notably with regard to the slopes of the isotherms.

In order to characterize the nature of the gasliquid phase transition in this system we have analyzed our data to obtain the shape of the coexistence curve and the isothermal compressibility in the liquid and vapor phases and at the inflection points of the isotherms for temperatures above the critical temperature  $T_c$ . To obtain the shape of the coexistence curve we fit our pressure data by polynomials in  $\rho$  near each side of the coexistence curve. The intersection of the fitted curves with the measured pressure in the hori-



FIG. 3. Isothermal compressibility along the liquid and vapor sides of the coexistence curve and at the inflection points of the isotherms above the critical temperature, and the difference between the liquid and gas densities, as a function of  $|T-T_c|$ .

zontal portion of each isotherm was used to calculate the liquid-phase density  $\rho_l$  and the vaporphase density  $\rho_v$  for that temperature. The pressures of the coexisting liquid and gas phases at any given temperature are equal to within ±0.02 mdyn/cm, which is the limit of our accuracy. This strongly supports the idea that this system undergoes a true condensation. Values of the isothermal compressibility

$$\kappa_{T} \equiv \frac{1}{\rho} \left( \frac{\partial \rho}{\partial \Pi} \right)_{T}$$

were calculated directly from the fitted curves and evaluated for  $\rho = \rho_i$  and  $\rho = \rho_v$ . For temperatures greater than  $T_c$  the isotherms were also fit

TABLE I. Experimental values of coexisting densities and isothermal compressibility of a two-dimensional film of pentadecanoic acid spread on a pH-2 water substrate.

$T (T < T_c)$ (° C)	$\rho_{i}$ (molecules/10 <sup>4</sup> Å <sup>2</sup> )	$ ho_v$ (molecules/10 <sup>4</sup> Å <sup>2</sup> )	$(\kappa_T)_l$ (cm/dyn)	$(\kappa_T)_v$ (cm/dyn)	$T\left(T > T_{c}\right)$ (° C)	$(\kappa_T)_T > T_c$ (cm/dyn)
14.80	160.0	14.6	216.2	260.9	26.77	1381.9
20.03	122.4	16.3	214.8	399.9	27.45	518.9
21.96	105.7	17.2	260.2	692.1	28.23	346.2
23.72	80.5	19.6	561.4	1183.6	29.20	226.4
24.97	68.7	24.8	1037.8	2246.1	30.10	206.6
25.63	62.5	25.4	1805.3	3932.5	31.07	154.7
					32.75	100.1
					34.69	81.0

by polynomials in  $\rho$ ; the compressibility,  $(\kappa_T)_{T>T_c}$ , was evaluated at the inflection point of each isotherm. The results of this analysis are given in Table I.

An accurate determination of  $T_c$  by direct means was not possible; we chose  $T_c$  by fitting the isothermal compressibility to power laws of the form  $\kappa_0 |T - T_c|^{-\gamma}$  and by requiring that the exponents  $\gamma$ and  $\gamma'_i$ , describing the behavior above the critical point and along the liquid side of the coexistence curve, respectively, be equal. This resulted in the choice  $T_c = 26.27$  °C.

Figure 3 shows the isothermal compressibility along both sides of the coexistence curve and at the inflection points of the isotherms for  $T > T_c$  as a function of  $|T - T_c|$  using this choice of  $T_c$ . Figure 3 also shows the density difference  $\rho_{l} - \rho_{v}$  as a function of  $|T - T_c|$ . It fits a power law of the form  $B(T_c - T)^{\beta}$ , with  $\beta = 0.50$ . The value of  $(\kappa_T)_i$ at  $T_c - T = 11.47$  K deviates markedly from powerlaw behavior and was not included in the fit. This is a real effect and is not attributable to experimental error. The exponents describing the behavior of  $\kappa_T$  along all three thermodynamic paths studied and the exponent describing the density differences are predicted by mean-field theory to have the values 1.0 and 0.5, respectively; the data are in excellent agreement with these predictions. With  $T_c$  fixed, the standard errors for the exponents  $\gamma$ ,  $\gamma'_i$ ,  $\gamma'_v$ , and  $\beta$  are ±0.03, ±0.07, ±0.04, and  $\pm 0.03$ , respectively. In the range  $26.20 \le T_c$  $\leq$  26.30 °C the exponents are all equal to the meanfield values within these errors. In three-dimensional systems the quantity  $\rho^2 \kappa_T$  is observed to exhibit power-law behavior along the coexistence curve over a much wider temperature range than does  $\kappa_{\tau}$  itself.<sup>9</sup> For this system, however, we find  $\rho^2 \kappa_T$  to depart from power-law behavior on both sides of the coexistence curve, while  $\kappa_{T}$  does not. Mean-field theory also predicts that for any given value of  $|T - T_c|$ ,  $(\kappa_T)_{T > T_c} \simeq 2(\kappa_T)_l \simeq 2(\kappa_T)_v$ . For this system we find  $(\kappa_T)_{T > T_c} \simeq \frac{1}{2}(\kappa_T)_l \simeq \frac{1}{4}(\kappa_T)_v$ , and no reasonable choice of  $T_c$  eliminates this conflict. Although the disagreement might vanish very near  $T_c$ , we feel that it is more likely caused by the ability of the molecules to change their orientation relative to the water surface as the density is increased.<sup>10</sup>

Using the value of  $T_c$  determined above, we find that the coexisting densities obey the law of rectilinear diameters, i.e., our data are fitted by the equation

$$\rho_l + \rho_v = 2\rho_c + D(T_c - T)$$

to within an accuracy of ±4.1 molecules/10<sup>4</sup>Å<sup>2</sup>. The best-fit values of the parameters  $\rho_c$  and D are

 $\rho_{c} = 41.7 \pm 4.1 \text{ molecules} / 10^{4} \text{ Å}^{2}$ 

and

# $D = 8.2 \pm 0.2$ molecules/10<sup>4</sup> Å<sup>2</sup> K.

The errors quoted are the standard fitting errors with  $T_c$  fixed. The quantity  $(\partial \Pi / \partial T)_{\rho=\rho_c}$  may be evaluated directly from the measured pressures and shows no change as the critical point is approached, having the fixed value of  $6.7 \pm 0.05$ mdyn/cm K. This is in agreement with the behavior observed in three-dimensional fluid systems. Using this value of  $(\partial \Pi / \partial T)_{\rho = \rho_c}$  we obtained the critical pressure  $\Pi_c$  by interpolation between the isotherms at 26.77 and 25.63  $^{\circ}$ C using  $T_c = 26.27 ~^{\circ}$ C. This yielded the result  $\Pi_c = 174 \text{ mdyn/cm}$ . Our values for the quantities  $\rho_c$ ,  $T_c$ ,  $\Pi_c$ , and  $(\partial \Pi / \partial T)_{\rho=\rho_c}$ may be compared with those of Hawkins and Benedek, who used an extrapolation procedure to obtain the values 29 molecules/ $10^4$  Å<sup>2</sup>, 26.9 °C, 145 mdyn/cm, and 8 mdyn/cm K, respectively. The densities at which the supercritical isotherms have their inflection points are scattered somewhat about the critical density but show no systematic departure from it.

Our numerical results may be summarized as follows:

$$\begin{split} (K_T)_v &= 2.73 \times 10^3 (T_c - T)^{-0.97 \pm 0.04} \, \mathrm{cm/dyn}, \\ (K_T)_I &= 1.25 \times 10^3 (T_c - T)^{-0.98 \pm 0.07} \, \mathrm{cm/dyn}, \\ (K_T)_{T>T_c} &= 6.73 \times 10^2 (T - T_c)^{-0.98 \pm 0.03} \, \mathrm{cm/dyn}, \\ \rho_I - \rho_v &= 41.9 (T_c - T)^{0.50 \pm 0.03} \, \mathrm{molecules}/10^4 \, \mathrm{\AA}^2, \\ \rho_I + \rho_v &= (83.4 \pm 8.2) \\ &+ (8.2 \pm 0.2) (T_c - T) \, \mathrm{molecules}/10^4 \, \mathrm{\AA}^2, \\ \left(\frac{\partial \Pi}{\partial T}\right) &= 6.7 \pm 0.05 \, \mathrm{mdyn/cm} \, \mathrm{K}, \end{split}$$

$$\rho_c = 41.7 \text{ molecules}/10^4 \text{ Å}^2,$$

$$T_{c} = 26.27 \,^{\circ}\mathrm{C},$$

 $\Pi_c = 174 \text{ mdyn/cm}.$ 

Our results are quite different from those of Hawkins and Benedek, especially with regard to the slopes of the isotherms throughout the entire region studied. For any given value of  $\rho_I - \rho_v$ , our values for the isothermal compressibility are from 10 to 20 times larger than theirs. In attempting to discover the causes for the different behaviors found in the two experiments we can find only two ways in which our experiment differed significantly from theirs: These are with regard to cleaning the water surface and controlling the pH of the substrate. After sweeping the surface they allowed contaminants to accumulate for approximately  $\frac{1}{2}h$ , after which time the pressure due to contamination "saturated" at ~25 mdyn/cm, and they found the rate of contamination to decrease substantially.<sup>11</sup> During the next hour the contaminant pressure in their experiment rose to ~30 mdyn/cm. We observed a very similar effect before our extensive cleaning efforts, but we feel that the "saturation" of contamination pressure may well be due to condensation of the contaminants into nongaseous phases. This view is supported by the fact that we observed much higher contamination pressures to be reached after approximately 12 h. For this reason it is not possible to estimate accurately the density of contaminant molecules present in the experiment of Hawkins and Benedek. An even more likely cause for the different experimental results lies in control of the substrate pH. Pentadecanoic acid is a weak acid and, although its dissociation constant does not seem to have been measured, other acids differing only in the length of the hydrocarbon tail have dissociation constants which vary slowly and regularly with chain length.<sup>12</sup> From these data we estimate the dissociation constant of pentadecanoic acid to be  $pK_a = 5.6$ . Consequently, when spread on a neutral substrate, the film will be 96% dissociated. When spread on a pure distilled-water substrate the degree of dissociation will not be well defined but will depend on factors such as the amount of CO, dissolved in the substrate. In the dissociated state the molecules will react with metallic ions such as Ca<sup>++</sup>. which are generally present in the substrate. Such reactions might well modify the interactions between individual pentadecanoic acid molecules and

between the molecules and the substrate. If this happened one would expect the film pressure to change since it is known that the addition of a single CH<sub>2</sub> group to the hydrocarbon chain of this acid is sufficient to lower the vapor pressure<sup>4</sup> at 15 °C by ~100 mydn/cm. In order to prevent such effects we used pure HCl to reduce the substrate pH to 2. Under these conditions the film is only 0.03% dissociated. Further evidence for the importance of pH control is offered by our own observation that when using pure freshly distilled water with no pH control we obtained results fairly near our own, but that after the water had been stored for  $\sim 12$  h we obtained coexistence pressures more nearly in agreement with theirs. The observed pressures decreased continuously with time during this period, and we speculate that this could have been caused by the loss of CO<sub>2</sub> dissolved in the freshly distilled water, which would have made it somewhat acidic initially. We did not make further measurements because the film was not truly stable, but presumably it would become so if the water were stored for a sufficient length of time.

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