Measurements of the Equation of State of a Two-Dimensional Gas near Its Critical Point*

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We have experimentally determined the equation of state of a two-dimensional "gas" of pentadecylic-acid molecules moving on the surface of water. Our data provide conclusive evidence for the occurrence of a phase transition in this two-dimensional system, similar to the liquid-vapor transition displayed by three-dimensional pure fluids. We have demonstrated the existence of a critical point, determined the shape of the coexistence curve, and observed an increase in the isothermal compressibility near the critical point.

Using a new technique for the precise determination of surface pressures, we have measured, as a function of density and temperature, the pressure of the two-dimensional "gas" formed by pentadecylic-acid molecules moving along the surface of water. Our equation-of-state measurements strongly support previous evidence[1] for the occurrence of a "liquid-vapor" phase transition in this two-dimensional system and demonstrate, for the first time, the existence of a critical point for a system of insoluble, aqueous surfactant molecules. We have determined the approximate shape of the coexistence curve and have obtained values for the critical pressure, density, and temperature. We have also observed an increase in the two-dimensional, isothermal compressibility κ_T in the vicinity of the critical point and find that the dependence of κ_T upon the width of the coexistence curve, $\Delta\rho$, is consistent with a simple power law whose critical exponent agrees with the predictions of mean-field theory. We may analyze our data in terms of a mean-field equation of state whose parameters characterize the average interparticle attraction and the geometrical orientation of the molecules on the water surface.

The two-dimensional gas of our experiment is formed by applying molecules of pentadecylic acid, $CH_3(CH_2)_{13}COOH$, to the surface of distilled water. These surfactant molecules are confined to motion along the air-water interface by the opposing actions of their polar groups, COOH, which strongly attract the water, and their hydrocarbon chains, which prevent appreciable dissolution. We directly measure the two-dimensional pressure P exerted by these molecules against a barrier which confines their motion to a fixed area of water surface.

As shown in Fig. 1, a Teflon trough of dimensions $60\times15\times2$ cm^3 is filled with water to a level about 1 mm above the top surface of the trough. A rigid boom or "float" contacts the water surface across the width of the trough and serves to confine surfactant molecules to one end of the trough. The float is supported mechanically by a vertical torsion wire and is free to swing along the water surface in response to the pressure of surfactant molecules. In this configuration, the float acts as a two-dimensional piston. To prevent leakage of the surfactant molecules around the ends of the piston, two small grooves filled with mercury are located at the ends of the float, as shown in Fig. 1. The level of mercury is adjusted until the top surface of the mercury just touches the bottom of the float. The water surface then contacts the float all along its length between the two mercury seals as well as contacting one side of each seal. This technique prevents the passage of pentadecylic-acid molecules around the float but does not impede its motion. Hence the sensitivity of our apparatus is deter-

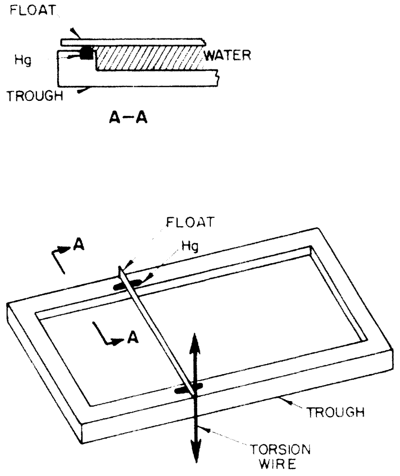

FIG. 1. Experimental apparatus for the measurement of surface pressures of insoluble, aqueous surfactants. Inset shows cross section of mercury seals.

mined only by the torsion constant of the wire and the accuracy to which we detect rotation of the float about the axis of the torsion wire.

In operation, a known density of pentadecylic-acid molecules is applied to the water surface at one end of the trough. The surface pressure of these molecules produces a torque which rotates the float. The angular orientation of the float is restored to its initial value by the application of an external magnetic field to a permanent dipole magnet located at the junction of the torsion wire and float. The current in the field coils is directly proportional to the pressure of the surfactant. Rotation is detected optically to an accuracy of 10^{-4} rad, and the torsion constant of the wire is chosen to permit the detection of changes in surface pressure as small as 2×10^{-4} dyn/cm. During a typical run, the surfactant density is incremented by a known amount and the balance renulled about thirty times for each experimental isotherm. We control temperatures to better than 0.1°C and maintain the environment at nearly saturated humidity. A detailed description of the device and its operation will be presented elsewhere.

Our measurements of the pressure P of the two-dimensional gas formed by pentadecylic-acid molecules on the surface of water are shown in Fig. 2 as a function of surfactant density ρ along nine isotherms in the temperature range $15 < T < 35$°C. At low densities, the isotherms converge to the ideal gas law $P=\rho k_{\mathrm{B}}T$, where k_{B} is Boltzmann's constant. At higher densities, the pressures depart from the ideal gas law, and, for temperatures ≤ 26.6°C, display behavior analogous to the liquid-vapor phase transition of pure fluids: Over a wide range of densities, the pressure is a function only of temperature. We have verified the density independence of the pressure along the flat portions of some isotherms to an accuracy of 2×10^{-4} dyn/cm, an improvement in resolution of about a factor of 20 over the early observations by Adam and Jessop[1] of the surface pressure of pentadecylic acid at the single temperature 14.5°C. The measured density independence of P along portions of the isotherms suggests that, in these regions, a high-density, two-dimensional "liquid" phase (l) coexists with a lower-density, two-dimensional "vapor" phase (v). The densities ρ_l and ρ_v of the coexisting phases are represented by the end points of the flat portions of the isotherms. The coexistence curve is shown in Fig. 2 as a smooth line connecting these end points.

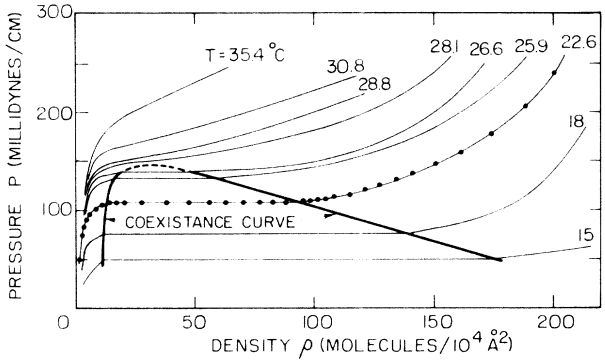

FIG. 2. Measurements of the pressure P of the two-dimensional gas formed by pentadecylic-acid molecules confined to motion on the surface of water as a function of surfactant density ρ along nine isotherms in the vicinity of the critical point.

The width of the coexistence curve, $\Delta\rho=\rho_l-\rho_v$, decreases with increasing temperature, until, for temperatures greater than a critical value T_c, there is no longer the possibility of two coexisting phases of the type observed below T_c. From a smooth extrapolation of both sides of the coexistence curve and from the value $dP/dT=8\pm1$ mdyn/cm deg, consistent with our pressure measurements in the two-phase region, we estimate $P_c=145\pm10$ mdyn/cm, $\rho_c=29\pm3$ molecules/10^4 Å^2, and $T_c=26.9\pm0.2$°C. In this system there is no visible meniscus whose disappearance could be used to determine the location of the critical point more precisely.

The most striking features of the equation-of-state measurements shown in Fig. 2, apart from the existence of a critical point, are the extreme asymmetry of the coexistence curve and the observed increase of the isothermal compressibility κ_T in the vicinity of the critical point. From experimental and theoretical investigations of critical phenomena,[2] we expect that, along the coexistence curve in the vicinity of the critical point, κ_T and $\Delta\rho$ depend upon the temperature difference $\Delta T=T_c-T$ through simple power laws with critical exponents γ and β respectively: $\kappa_T\sim(\Delta T)^{-\gamma}$ and $\Delta\rho\sim(\Delta T)^{\beta}$. Because of our imprecise knowledge of T_c, it is difficult to compare our data with these predictions. However, we may eliminate ΔT from the above relations to obtain $\kappa_T\sim(\Delta\rho)^{-\gamma/\beta}$, a prediction which is accessible to direct experimental verification. While we are limited by this approach to the investigation of the ratio of two exponents, the particular exponent ratio γ/β differs widely for various

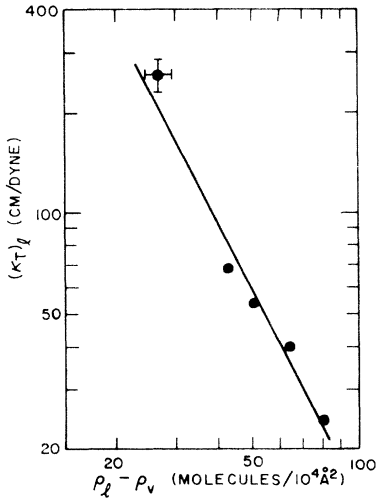

FIG. 3. Experimentally deduced values of the isothermal compressibility κ_T along the liquid side of the coexistence curve as a function of the full width of the coexistence curve, $\Delta\rho$. Straight line is of slope 2.0. The reduced temperature ϵ ranges from approximately 0.001 to 0.018 for the points shown.

theoretical models and experimental systems. In mean-field theory the ratio is 2 in all dimensions; for most three-dimensional theories and experiments it lies in the range 3.7 to 4.1, and for the two-dimensional Ising model solved by Onsager[3] and Yang[4] the ratio is 14.

Our experimentally deduced values of κ_T along the liquid side of the coexistence curve as a function of $\Delta\rho$ are graphed logarithmically in Fig. 3. Within experimental error, the data points define a straight line of slope 2.0 ± 0.3, in striking agreement with the predictions of mean-field theory.[5] It is, of course, possible that our measurements do not extend sufficiently close to T_c for the critical exponents to have assumed their asymptotic values. We note, however, that pentadecylic-acid molecules do possess permanent dipole moments whose long-range interactions may account for the apparent mean-field behavior of the exponents. Calculations of Fisher and co-workers[6,7] indicate that, in two-dimensional systems, a potential of the dipole form r^{-3} is just sufficient to produce mean-field exponents, even in the limit $\Delta T \to 0$.

Guided by the apparent mean-field behavior of the critical exponents, we have analyzed our data in terms of a mean-field equation of state of the Van der Waals form, $P(\rho, T) = \rho k_B T/(1 - b\rho) - a\rho^2$. The parameter a represents the average interparticle attraction per molecule. The two-dimensional "excluded volume" b characterizes the average area of water surface occupied by a surfactant molecule. If a and b are taken as constants, this equation, in conjunction with the Maxwell equal-area construction, predicts a rather symmetric coexistence curve, in marked disagreement with our experimental measurements. However, in applying an equation of state of the Van der Waals form to our two-dimensional system, we may argue, on physical grounds, that the parameter which describes the excluded area must be regarded as a decreasing function of density. At low surfactant densities, the long, hydrocarbon chains of the pentadecylic-acid molecules lie *on* the water surface. However, as the surfactant density is increased, the polar groups remain in contact with the water while the hydrocarbon chains rise off the surface and tend to align in the vertical direction,[8] substantially reducing the average area of surface occupied by the molecules. In fact, using the Maxwell construction principle in the two-phase region, we may fit our data along all isotherms using a single, empirically deduced function $b(\rho)$ whose behavior is consistent with our physical expectations. If we model the surfactant molecules as rods of the same length and volume as molecules of pentadecylic acid, we find that the value of $b(\rho)$ at low densities, $b(\rho = 0) = 225$ Å^2, is consistent with the excluded area of rods lying on the water surface, while the value of $b(\rho)$ at very high densities, $b(\rho \approx 400$ molecules/10^4 Å^2) $= 22$ Å^2, agrees with the excluded area of rods aligned perpendicular to the surface. At intermediate densities, $b(\rho)$ varies smoothly and monotonically between the high- and low-density limits. [For the best fit to our data, we must also allow a ($\approx 6 \times 10^{27}$ dyn cm^3) to depend weakly on ρ and T for $\rho < 20$ molecules/10^4 Å^2. However, the equation of state is far more sensitive to values of b than to those of a.]

While this analysis is semiempirical, it strongly suggests that the extreme asymmetry which we observe for the coexistence curve of pentadecylic acid is directly related to the ability of the surfactant molecules to alter their effective hard-core diamteres appreciably by vertical orientation of their hydrocarbon chains. We may also conclude, at least over the range of the present data, that this two-dimensional system exhibits mean-field critical behavior consistent with the existence of long-range interactions.

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[1] N. K. Adam and G. Jessop, Proc. Roy. Soc., Ser. A 110, 423 (1926).

[2] L. P. Kadanoff *et al.*, Rev. Mod. Phys. 39, 395 (1967).

[3] L. Onsager, Phys. Rev. 65, 117 (1944).

[4] C. N. Yang, Phys. Rev. 85, 809 (1952).

[5] Along the liquid side of the coexistence curve, the quantity $\rho^2\kappa_T$, in contrast to κ_T itself, does not depend on $\Delta\rho$ according to a simple power law over the full density range of Fig. 3, although the slope of $\rho^2\kappa_T$ appears to approach 2 asymptotically near ρ_c. Along the vapor side of the coexistence curve, $\rho^2\kappa_T$ obeys a power law (exponent 1.8 ± 0.3) over a wider range of densities than does κ_T alone. More extensive experimental data are needed to investigate the existence of a natural thermodynamic variable for the compressibility.

[6] M. E. Fisher, S. Ma, and B. G. Nickel, Phys. Rev. Lett. 29, 917 (1972).

[7] M. E. Fisher and A. Aharony, Phys. Rev. Lett. 30, 559 (1973).

[8] I. Langmuir, J. Amer. Chem. Soc. 39, 1848 (1917).

Transient Self-Focusing in a Nematic Liquid Crystal in the Isotropic Phase

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We have made the first quantitative experimental study of transient self-focusing in a Kerr liquid by propagating *Q*-switched laser pulses in an isotropic nematic substance which has a long orientational relaxation time. Our results show good qualitative, and occasionally quantitative, agreement with the existing theoretical calculations.

Self-focusing of light in a Kerr liquid has been a subject of extensive investigation.[1] It gives rise to the observed intense streaks and many other related phenomena. Quasi-steady-state self-focusing is now well understood. Most of the observed results can be explained satisfactorily by the picture of moving foci.[2,3] Transient self-focusing is however still in a state of confusion. There already exist a number of detailed numerical calculations on the subject,[4-6] but no quantitative experimental results are yet available to check these calculations. The reason is obvious. Transient self-focusing occurs when the laser pulse width W is shorter than or comparable to the relaxation time τ of the field-induced refractive index Δn. Since in ordinary Kerr liquids τ is in the picosecond range, picosecond pulses must be used in the transient studies.[7] Unfortunately, picosecond pulse technology is still in such a primitive stage that quantitative measurements are extremely difficult and expensive. Experiments on transient self-focusing would be so much easier if nanosecond pulses could be used, but then the medium should have a relaxation time τ in the 50-nsec range. This happens to be the case for liquid crystalline material in the isotropic phase.[8] In this paper, we would like to report the preliminary results of our experimental investigation on transient self-focusing in such a medium. Out results are in good agreement with the existing theoretical calculations.[5,6]

Let us first have a brief review on the theory of transient self-focusing. The phenomenon is presumably governed by the equations

$$[\nabla^2 - (\partial^2/c^2\partial t^2)(n_0 + \Delta n)^2]E = 0, \tag{1}$$

$$(\tau\,\partial/\partial t + 1)\Delta n = \Delta n_0, \tag{2}$$

where n_0 is the linear refractive index and $\Delta n_0 \cong n_2|E|^2$, n_2 being a constant. The solution of Eqs. (1) and (2) has been obtained numerically.[4-6] It can be described qualitatively from the following physical reasoning. If the input pulse is short, then Δn can never reach its steady-state value. We can write

$$\Delta n(z,\zeta) = (1/\tau)\int_{-\infty}^{\zeta} n_2|E(z,\eta)|^2 \exp[-(\zeta-\eta)/\tau]\,d\eta,$$

where $\zeta = t - zn_0/c$ is the local time. For an input pulse width comparable to τ, Eq. (3) shows that the later part of the pulse may see a larger Δn. Consequently, different parts of the pulse propagate differently in the medium as shown in Fig. 1.[6] The front part (a, b) of the pulse sees little induced Δn and diffracts accordingly. It however leaves a sufficiently large Δn in the