Phase Transitions of Liquid-Crystal Films on an Air-Water Interface

Jiuzhi Xue,[1],[2] C.S. Jung,[1],[3] and Mahn Won Kim[1]

[1]*Exxon Research and Engineering Company, Route 22 East, Annandale, New Jersey 08801*
[2]*Department of Physics, Princeton University, Princeton, New Jersey 08544*
[3]*Department of Physics and Optical Engineering, Chungjoo University, Chungjoo, Korea*

(Received 16 April 1992)

Surface-balance, ellipsometry, and optical second-harmonic-generation techniques are employed to investigate the phase transitions of liquid-crystal 4'-n-octyl-4-cyanobiphenyl films on an air-water interface. We have found, for the first time, a distinctive first-order phase transition between a stable monolayer phase and a stable 3-layer phase of the liquid-crystal film.

A water surface can support many types of molecules consisting of a nonpolar tail and a polar group. Studies on relatively flexible surfactants and polymers on the air-water interface have considerably broadened our understanding of the structures and properties of a 2-dimensional gas, liquids, and various ordered monolayer phases that exist in nature [1–6]. Experimentally, it has been observed that only monolayers formed by these flexible molecules on the air-water interface are thermodynamically stable.

Most thermotropic liquid-crystal (LC) molecules are small rodlike lipids that are insoluble in water. These short rigid rods, whose interparticle interactions are considerably simpler than that between surfactants and polymers, may therefore form different phases on the air-water interface and are ideal to study. A markedly different feature between bulk LCs, flexible surfactants, and polymers is that often bulk LCs have smectic phases. A particularly interesting question is therefore the propagation of layer orderings of LCs on the air-water interface beyond a stable monolayer film. Understanding the influence of a substrate on the structures and phase behavior of LCs is by itself of fundamental importance from both a purely scientific and a technological point of view [7, 8].

In this Letter, we report our studies on 4'-n-octyl-4-cyanobiphenyl (8CB), situated on the air-water interface. Our work is different from the other studies in that the LCs we employed are chemically stable and we study the detailed phase behavior of the films [9, 10]. Using surface-balance [5], ellipsometry [11], and optical second-harmonic-generation (SHG) techniques [4], we have measured the surface pressure, density, molecular alignment, and the polar ordering of the LC film as a function of area per molecule. We have found, for the first time, that a LC monolayer on an air-water interface undergoes a first-order transition to a stable phase that is composed of a monolayer plus an interdigitated bilayer (3-layer film). Formation of the stable 3-layer film is due to a delicate balance between molecular interactions in the system.

A monomolecular film can be in different states depending on the density of the molecules on the surface. The surface pressure Π, the reduction of surface tension of water due to the existence of molecules on the surface,

as a function of area per molecule, gives the equation of state and can be measured directly using a surface balance apparatus. A film of organic monolayer on the air-water interface is, in general, birefringent with its optic axis perpendicular to the interface [12, 13]. If the thickness of the film d is very small compared to the wavelength of the laser beam λ, then the ellipsometry signal is proportional to d, and is a complicated algebraic function of the refractive indices of air and water, the ordinary and extraordinary refractive indices of the film, and the angle of incidence of the laser beam [13].

The molecular alignment and the polarity of molecules at an interface can be most directly probed using optical SHG. The SHG signal is nonzero only when the centrosymmetry is broken in the dipole approximation. In this case, the interface breaks the symmetry and we expect a nonzero SHG signal that is dipolar in nature and that provides information about the molecular arrangement in the immediate vicinity of the interface. For LC molecules with a relatively rigid polar group and a floppy tail, the molecules in the bulk form pairs with polar groups pointing antiparallel to each other. In general, the quadrupole moment of the pairs is not zero, and, in an ordered phase, a contribution to the SHG signal from these quadrupoles is expected.

A cyanobiphenyl LC molecule is composed of a hydrophilic polar (cyano) head group and a hydrophobic alkyl tail group. In our experiments, 15 mg of LC are dissolved in 10 ml of hexane and the solution is spread on an air-water interface in a Langmuir trough using a microsyringe. The hexane quickly evaporates and the LCs are left on the interface with their head group pointing towards the water. Typically, 35 ± 0.5 μl of the solution is spread on the interface. The area per molecule A or the number density of LC molecules on the interface, which is determined to within 5% , is subsequently modified by changing the total area occupied by the LC film. The temperature of the Langmuir trough is controlled to within 0.2 °C.

We measure the pressure of the film by slowly compressing and then expanding the film at the same rate. At a sufficiently slow speed of about 0.2 cm^2/s, the compression and expansion process yields the same equilibrium

pressure in the film. Figure 1 shows our typical results of Π as a function of A at room temperature where the bulk material is in smectic-A (S_A) phase. In contrast to isotherms observed for a majority of insoluble polymers or surfactants on the air-water interface [4–6], we find that after a rapid increase in Π at relatively large A, Π saturates at intermediate A (12 Å^2 < A < 40 Å^2), increases sharply as A is reduced, and then slowly increases again as A is further reduced.

At very large A, the LC molecules on the interface should be in gas phase [10]. As A is reduced, the film goes through a first-order phase transition to a liquid phase. In regions where A is slightly greater than 50 Å^2 (region I), Π is about 0.1 dyn/cm and constant (first plateau region), indicating a coexistence of gas and liquid phase. The LC film in the region 48 Å^2 > A > 41 Å^2 (region II), where the first significant increase in Π occurs, is postulated to be a homogeneous monolayer liquid phase [4–6], in analogy to the liquid expanded phase of insoluble polymers and surfactants on the air-water interface. Combined with the facts that in bulk the LC is in the S_A phase [14] and the polar group is pointing towards water, we further postulate that this phase is a ferroelectric monolayer phase with molecules roughly perpendicular to the interface. It is interesting to note that the area per molecule in this phase is about twice the value for molecules in the bulk phase [14], and is approximately the size of a benzene ring. This suggests that the dominant contribution to the pressure in this region is probably due to the steric interactions between the "core" of the liquid crystals and therefore should be fairly insensitive to temperature.

As A is reduced, the pressure first remains constant (region III) and then rises sharply (region IV). This isotherm indicates that there exists another stable phase at the smaller A (region IV), and the transition between this phase and the proposed homogeneous monolayer phase is first order. We find that the transition to smaller
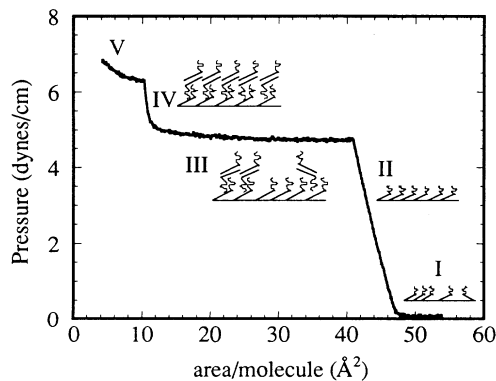
A phase occurs at 11.4 Å^2, which is too small for all the molecules to remain on the interface. Since the LC is not soluble in water, molecules are forced to go into the third dimension, i.e., forming additional layers on top of the first monolayer. By considering the packing of the molecules, we find that the additional (second) layer formed is unlikely a monolayer [15, 16]. However, if we assume that the second layer is an interdigitated bilayer, we then find that A for the molecules in the second layer is 22.6 Å^2, a value that is very close to that for the bulk material [14]. We postulate from these isotherm measurements that the 8CB film in the smaller A regime is a 3-layer film, i.e., an interdigitated bilayer on top of a ferroelectric monolayer adjacent to the interface.

Along with the isotherms, we simultaneously measured the ellipsometry signal I_e of the films. In Fig. 2 we plot a typical result. In region I, we find that I_e is fluctuating between nearly zero and a constant, a signature of the coexistence of the gas and liquid [4–6]. In region II, I_e is steady and increases slightly due to a slight increase in density, consistent with the picture that the film is a homogeneous monolayer film. In region III, we find that I_e is fluctuating between the values for a monolayer and that for the film in region IV, and therefore in accordance with the isotherms for this region, a monolayer is in coexistence with a 3-layer phase, and further confirming that the transition between the two phases is first order.

In region IV, we find again that I_e is steady, indicating that the film is homogeneous. We further find that the phase shift in this region is 2.12 ± 0.05 times the value for the monolayer. This ratio is suprisingly small, because if all molecules contribute to the phase shift in the same way, we would expect the ratio to be at least 3. To try to understand this, we first carefully measured the ellipsometry signal for cyanobiphenyl materials with different chain lengths and thus separated the contributions from the tails and the head group [11]. We find that for the
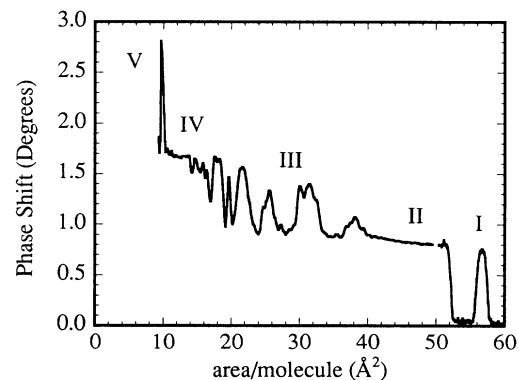

FIG. 1. Typical Π-A diagram for 8CB film on the air-water interface. LC molecular arrangements are also sketched in corresponding regions, with solid lines representing the polar group of the molecules.

FIG. 2. Ellipsometry signal (phase shift) as a function of area per molecules for 8CB on air-water interface at room temperature. The figure is obtained by combining data from two measurements, which are separated by a gap in the horizontal axis.

monolayer 8CB the head groups contribute nearly 70% to the total phase shift to the film. This can be understood as being due to the unpaired dipoles of the molecules, and thus the monolayer is effectively highly birefringent. The molecules in the second layer, however, form interdigitated bilayers, and the head groups form pairs and are not so susceptible along their long axes; thus the bilayer is less birefringent. To estimate the phase shift due to the interdigitated bilayer, we assume that there is only the bilayer present at the air-water interface with the optical axis perpendicular to the interface. We further assume that the refractive index for the bilayer is the same as the value for the bulk material [17] and that the thickness of the bilayer is 1.4 times the molecular length. Under our experimental conditions, we calculate and find that the phase shift due to such a hypothetical bilayer is 1.326°. If we make the crude approximation that the phase shift of the 3-layer film is the sum of that due to the bilayer and the monolayer, we find that the phase shift ratio between the 3 layer and monolayer is 2.51, suggesting that the model is at least qualitatively correct.

When A is reduced below 11.4 Å^2, we find that no stable 5 layers or other multilayer films exist (region V), as indicated by a continuous increase in Π, and an arbitrary fluctuation in I_e above the values for a 3-layer film. In fact, very thick patches of the LC film, which are visible to the naked eye, are observed in this regime.

We further studied the phase transition behavior of the system using optical SHG. Figure 3 shows the optical SHG obtained for 45°-input/s-output polarization combination. In region I, the SHG data show similar fluctuating behavior to that of the ellipsometry data, as expected for the coexistence phase of gas and liquid. When A is increased to the gas phase, the SHG signal is small and constant. In region II, the SHG signal remains nearly constant, further indicating that the film is in a homoge-
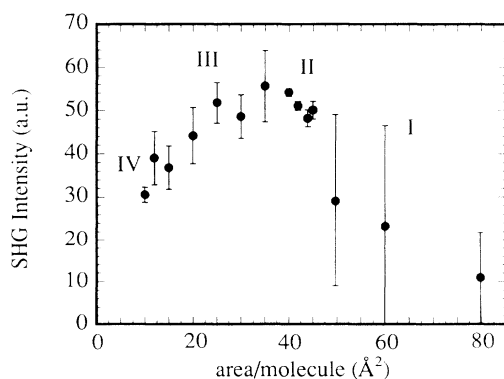
neous monolayer region.

Assuming the molecules are simply tilted with respect to the interface normal and that they reside on a cone, the hydrophilic polar group of the molecules makes an angle θ with the interface normal. The nonlinear susceptibility components of the film can then be calculated and compared with the SHG data. From our measurement, we find that $\theta = 62°$ in the monolayer phase, i.e., the polar group of 8CB is tilted 62° away from the interface normal. If we assume that the two phenyl rings are perpendicular to each other, and the molecules rest on the interface purely due to steric interactions, we estimate the angle between the polar group and the interface layer normal to be $\theta = 68.5°$ [14]. Thus the steric interaction may be dominant in determining the tilt angle of the molecules near the interface.

In region III, where we postulated that the film is in the coexistence state of a monolayer and a 3-layer phase, in addition to the contribution from the dipoles of the monolayer adjacent to the interface, we expect a quadrupole contribution to the SHG signal from the interdigitated bilayer on top of the monolayer. This quadrupole contribution to the nonlinearity of the LC has been shown to be significant [16]. The coexistence of the two phases indicates that we should expect the SHG signal to fluctuate above (or below, in the case where the dipolar and quadrupolar contributions cancel each other) a constant. As we can see in Fig. 3, we indeed find that the SHG intensity shows slight fluctuations in this region. As we approach region IV, the fluctuation in SHG intensity becomes less frequent and eventually in region IV, the SHG intensity is again nearly a constant, in agreement with the region being a homogeneous 3-layer phase.

We thus find that the isotherm, the ellipsometry, and the SHG measurements all give self-consistent results, and that the 8CB film on the air-water interface exhibits a first-order transition between a stable homogeneous monolayer liquid phase and a 3-layer phase.

The phase diagram of bulk 8CB is crystal (21.5 °C), S_A (33.5 °C), nematic (40.5 °C), and isotropic. The above phase behavior is observed from 10 to 38.7 °C, i.e., in a temperature range much wider than that for the smectic-A phase. At extremely low temperatures, e.g., 4.0 °C, LC films on the interface are no longer stable, and LCs aggregate. Thick patches of LC aggregates are visible. At 42.5 °C, on reducing the area per molecule, both static pressure and the ellipsometry signal continuously increase after a stable monolayer, making it difficult to determine if there is still layered structure beyond the monolayer.

While there is as yet no detailed theoretical work to explain the observed phenomena, it appears that the delicate balance between the work of adhesion of the molecule to the water and the work of cohesion between the molecules is responsible for this novel phase behavior

FIG. 3. SHG intensity as a function of area per molecule for 8CB at room temperature. The polarization combination is chosen to be 45°-in/s-out for maximum signal-to-noise ratio. The vertical bars indicate the range of the fluctuating signal.

[6, 16]. The work of adhesion is a combination of the hydrophilic force and hydrophobic hydration between the molecules and water. The formation of a stable monolayer film of 8CB on the air-water interface can be understood in a conventional way since there is a strong attractive interaction between the molecule's polar group and water. If we keep the work of adhesion roughly constant and change the work of cohesion by changing the length of the hydrophobic tail, we expect possible changes in the stability of the LC monolayer film on the interface, as we have observed experimentally [18].

As in a surfactant or an emulsion system, water can penetrate some certain distance up into the alkyl chain part of the molecules [19, 20]. If the alkyl chain is relatively short, then there may be a large amount of water molecules concentrated near the interface of the monolayer and air. Although it will not stabilize another monolayer like the first layer due to the hydrophilic nature of the polar head group of the molecules, water accumulated near the monolayer-air interface may be enough to attract the polar groups of a bilayer of the LC molecules. Formation of a stable 3-layer film seems to suggest that this is indeed the case for 8CB and for a few of its homologue series with similar alkyl chain lengths [18]. It should be noted that the LC molecules also alter the water concentration profile, which can be directly probed by neutron scattering techniques; in addition, we expect that water should condense near the head group region of the interdigitated bilayer. Experimentally, we also find that the monolayer and the 3-layer films do not wet oil (hexane, hexadecane, etc.), further suggesting that there is water in the films.

In conclusion, we have observed a novel monolayer to a 3-layer phase transition of 8CB film on an air-water interface. The transition between the two phases is first order. We find that these interface stabilized phases exist in a temperature range much wider than that of the smectic phase of the bulk material. We argue that these phenomena are due to a delicate balance between the intermolecular interactions.

[1] N.K. Adam, *Physics and Chemistry of Surfaces* (Oxford Univ. Press, London, 1941).

[2] K. Shinoda, T. Nakagawa, B.I. Tamamushi, and T. Isumura, *Colloidal Surfaces* (Academic, New York, 1963).

[3] X. Qiu, J. Ruiz-Garcia, K.J. Stine, C.M. Knobler, and J.V. Sellinger, Phys. Rev. Lett. **67**, 703 (1991).

[4] Th. Rasing, Y.R. Shen, M.W. Kim, P. Valint, Jr., and J. Bock, Phys. Rev. A **31**, 537 (1985).

[5] B.B. Sauer, H. Yu, M. Yazdanian, G. Zografi, and M.W. Kim, Macromolecules **21**, 2332 (1988).

[6] M.W. Kim, S.N. Liu, and T.C. Chung, Phys. Rev. Lett. **60**, 2745 (1988).

[7] P. Sheng, Phys. Rev. A **26**, 1610 (1982).

[8] See, for example, J. Cognard, *Alignment of Nematic Liquid Crystals and Their Mixtures* (Gordon and Breach, London, 1982).

[9] B. Rapp and H. Gruler, Phys. Rev. A **42**, 2215 (1990).

[10] Th. Rasing, G. Berkovic, Y.R. Shen, S.G. Grubb, and M.W. Kim, Chem. Phys. Lett. **130**, 1 (1986).

[11] M.W. Kim, B.B. Sauer, H. Yu, M. Yazdanian, and G. Zografi, Langmuir **6**, 236 (1989).

[12] K.B. Blodgett and I. Langmuir, Phys. Rev. **51**, 964 (1937).

[13] R.M.A. Azzam and N.M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1987).

[14] A.J. Leadbetter, R.M. Richardson, and C.N. Colling, J. Phys. (Paris), Colloq. **36**, C1-37 (1975).

[15] D.H. Van Winkle, S.B. Dieker, and N.A. Clark, J. Chem. Phys. **91**, 5212 (1989).

[16] H. Hsiung and Y.R. Shen, Phys. Rev. A **34**, 4303 (1986).

[17] R.G. Horn, J. Phys. **39**, 105 (1978).

[18] J.-Z. Xue and M.W. Kim (to be published).

[19] J. Shelley, K. Watanabe, and M.L. Klein, Int. J. Quantum Chem. **17**, 103 (1990).

[20] *Surfactants in Solutions*, edited by K.L. Mittal and B. Lindman (Plenum, New York, 1984), Vol. 1.