Observation of Molecular Reorientation at a Two-Dimensional-Liquid Phase Transition

Th. Rasing and Y. R. Shen

Department of Physics, University of California, Berkeley, California 94720, and Center for Advanced Materials,
Lawrence Berkeley Laboratory, Berkeley, California 94720

and

M. W. Kim and S. Grubb

Exxon Research and Engineering Company, Annandale, New Jersey 08801

The structure of a monolayer of pentadecanoic acid near the liquid-expanded–liquid-condensed phase transition at a water-air interface is studied by optical second-harmonic generation. The results show that this transition is accompanied by a reorientation of the molecules and that the two phases are separated by an inhomogeneous coexistence region on the isotherms.

The question of phase transitions in two dimensions is of great fundamental interest and has therefore drawn a considerable amount of attention.[1,2] Insoluble monomolecular layers at a water-air interface provide a quite ideal two-dimensional model system with an isotropic substrate and an easily controllable density of molecules. At low densities they often exhibit a two-dimensional gas behavior,[3] whereas at higher densities transitions to liquid and solid states can be found. In many systems, the liquid phase is further divided into the so-called liquid-expanded (LE) and liquid-condensed (LC) phases.[4] Though observed and intensively studied, the nature of the LE-LC phase transition is still controversial. It is not clear whether the transition is of first or higher order, and whether it is connected with a change in the translational order (melting) or with a "melting" of only the hydrocarbon chain, which would give rise to a liquid–oriented-liquid type of phase transition.[1,4] Experimental data are almost exclusively limited to surface-tension measurements, and for their interpretation various assumptions about the molecular orientation must be made. So far as we know, no direct experimental measurement of the molecular orientation in such a system has ever been reported.

In this paper we will demonstrate how we can use optical second-harmonic generation (SHG) to measure the molecular orientation of a monolayer of pentadecanoic acid (PDA) [$CH_3(CH_2)_{13}COOH$] near its LE-LC transition at a water-air interface. By simultaneously measuring the surface pressure versus surface molecular area we can show for the first time that this LE-LC transition is accompanied by a reorientation of the molecules and that the two phases are separated by an inhomogeneous coexistence phase.

The effectiveness of SHG as a surface probe stems from the fact that in the electric dipole approximation SHG is forbidden in centrosymmetric media but allowed at the interfaces where this inversion symmetry is necessarily broken. Apart from the intrinsic high spectral and time resolution, SHG is a unique surface probe because of its versatility: It can be used at solid-vacuum, solid-solid, solid-air, solid-liquid, and liquid-air interfaces, as has been shown recently.[5-9]

The surface nonlinear susceptibility $\chi_s^{(2)}$ arising from a monolayer of adsorbates can be written as

$$\chi_s^{(2)} = N_s \langle \alpha^{(2)} \rangle, \tag{1}$$

where N_s is the surface density of the molecules and $\langle \alpha^{(2)} \rangle$ is the nonlinear polarizability averaged over the molecular orientational distribution. If $\alpha^{(2)}$ is dominated by a single component $\alpha_{\xi\xi\xi}^{(2)}$ along a molecular $\hat{\xi}$ axis, and the latter is randomly distributed in the azimuthal plane, the nonvanishing components of $\chi_s^{(2)}$ can be written as[6]

$$\chi_{zzz}^{(2)} = N_s \langle \cos^3\theta \rangle \, \alpha_{\xi\xi\xi}^{(2)},$$

$$\chi_{zxx}^{(2)} = \chi_{zyy}^{(2)} = \chi_{xzx}^{(2)} = \chi_{yzy}^{(2)}$$

$$= \tfrac{1}{2} N_s \langle \sin^2\theta \cos\theta \rangle \, \alpha_{\xi\xi\xi}^{(2)}, \tag{2}$$

where θ is the polar angle between $\hat{\xi}$ and the surface normal $\hat{z}$. It follows from Eq. (2) that a measurement of the ratio of any two linear combinations of $\chi_{zzz}^{(2)}$ and $\chi_{zxx}^{(2)}$ can yield a weighted average of θ.[10]

Monolayers of PDA were prepared by spreading a solution of PDA in petroleum ether or hexane on a thoroughly cleaned water surface (pH$=2$). The trough was made out of glass and the edges of it were coated with paraffin. The surface density of molecules was controlled by a movable Teflon barrier and the surface tension was measured by a Wilhelmy plate.[11]

Figure 1 shows the measured surface pressure π as a function of the surface area per molecule A for PDA on a pH$=2$ water substrate at various temperatures. The sharp kinks in the middle of each π-A curve sig-
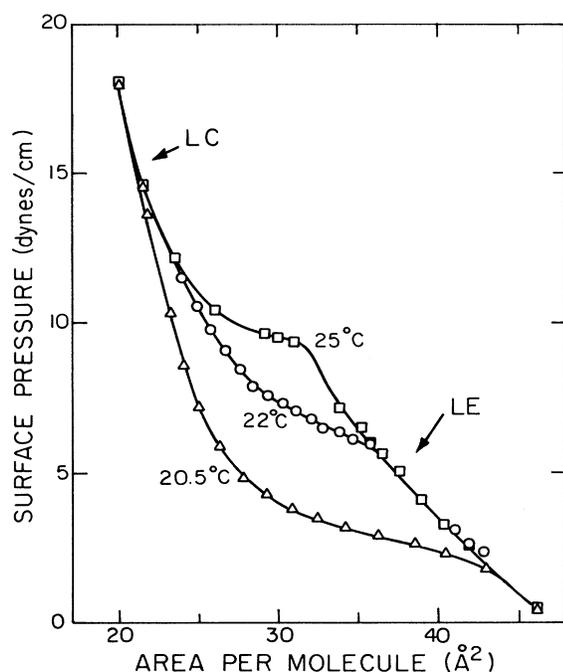
FIG. 1. Surface pressure of PDA as a function of the area per molecule on a water surface of $pH = 2$ for various temperatures.

FIG. 2. Tilt angle θ between the molecular axis and the surface normal as a function of the surface density of PDA on water at 25 °C. The dashed line is an extrapolation through the data points.

nals the onset of the transition between the LE and LC phases. As can be seen in the figure the transition point is strongly temperature dependent.

For the SHG measurements we used the frequency-doubled output of a Q-switched neodymium-doped yttrium aluminum garnet laser at 532 nm with a 7-nsec pulse width as the pump beam. Because of higher-order contributions, there was a nonnegligible signal from the bare water proportional to $|\chi_w^{(2)}|^2$, while the signal from the adsorbate-covered surface was proportional to $|\chi_w^{(2)} + \chi_x^{(2)}|^2$. Both could be measured separately. In order to deduce $\chi_s^{(2)}$, we need to know the phase difference between $\chi_s^{(2)}$ and $\chi_w^{(2)}$. This was obtained by interference of both signals with that from a quartz plate excited by the same pump beam. We found that within the experimental accuracy ($\pm 3°$) the phase difference was zero. This agrees with the fact that both ω and 2ω are far away from resonances in water and PDA, a reason which also explains why the observed signals were so small. Using a pump energy of ~ 20 mJ per pulse focused to 0.4 cm^2, we obtained a SH signal of 2–3 photons/pulse from the bare water and an additional ~ 0.4 photon/pulse from PDA molecules at $\pi = 15$ dyn/cm.

We first found that $\chi_{zxx}^{(2)} = \chi_{xzx}^{(2)} = \chi_{zyy}^{(2)} = \chi_{yzy}^{(92)}$ and that the PDA monolayers were azimuthally symmetric. From this we conclude that the polarizability tensor $\alpha^{(2)}$ is indeed dominated by a single component $\alpha_{\xi\xi\xi}^{(2)}$
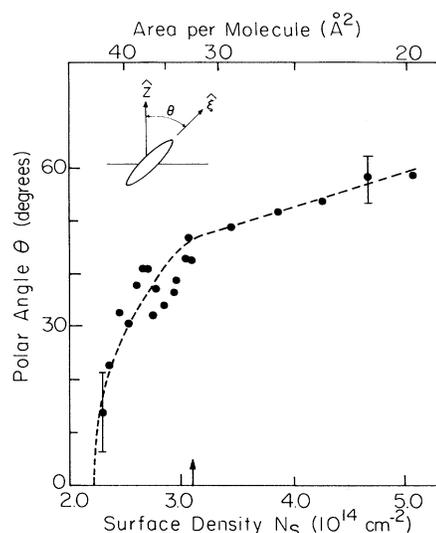
and that Eq. (2) can be applied in order to deduce its orientation. By comparing the SH signal from PDA with those from a pure hydrocarbon chain and from an alcohol of approximately the same chain length, we found that $\alpha_{\xi\xi\xi}^{(2)}$ arises mainly from nonlinearity along the C—OH bond. Thus, our measurements refer to the orientation of this polar bond. To obtain this value, we have assumed a δ-function distribution at θ, but random in the azimuthal plane.[10]

Figure 2 shows the results of our orientation measurements for PDA at 25 °C. In the LE phase, θ increases rapidly with increasing surface density, until the LE-LC transition sets in. Thereafter, it changes more slowly and almost linearly until it reaches a saturation value of $\theta \sim 60°$ for a full monolayer ($N_s = 5 \times 10^{14}/\text{cm}^2$).

These results agree with what one would expect. The polar C—OH bond will preferentially orient normal into the water. Indeed, if we extrapolate the experimental results in Fig. 2 to lower densities we find θ approaching 0 near the gas-LE transition[12] at $N_s = 2.2 \times 10^{14}/\text{cm}^2$. As the surface density increases in the LE phase, the steric interaction of the hydrocarbon chains of neighboring molecules becomes more important and tends to align the hydrocarbon chain toward, and hence to force the C—OH orientation away from, the surface normal. The increasing molecular interaction finally induces (at $N_s = 3.1 \times 10^{14}/\text{cm}^2$ for 25 °C) a phase transition to the LC phase.

Upon further compression, one arrives at a full, close-packed monolayer. The observed final angle of

$\theta \sim 60°$ can be simply understood from the picture that in the close-packed configuration, the straightened hydrocarbon chain has to orient along the surface normal and hence $\theta = 60°$ corresponds to a bond angle of $120°$ between the C—OH and the hydrocarbon chain, in agreement with the molecular structure. In fact, with a cylindrical cross section of $A_m = 18.1$ Å^2 for a hydrocarbon chain, a close-packed configuration leads to an area per molecule $A = 20.8$ Å^2 which agrees very well with the observed value of $A = 20$ Å^2 in the π-A diagram.

As seen in Fig. 2, the LE-LC transition occurs at $\theta = 43°$ for PDA at 25 °C. We have measured θ for other temperatures in the LE phase just before the transition point. The results given in Table I show that although the transition point A_c changes appreciably with temperature (more than 30% in the observed range) we find $\theta = 45° \pm 3°$ for all temperatures.

The variation of θ with the surface molecular density N_s in the LE phase can be well fitted by the relation $\theta \propto (N_s - N_{LE})^{1/2}$, where $N_{LE} = 2.2 \times 10^{14}/\text{cm}^2$ is the density at the beginning of the LE phase. This rather rapid increase of θ with N_s cannot be understood by considering the hydrocarbon chains as rigid rods. Neither the anchoring cross-sectional area of the molecules on the surface, which changes as $1/\cos(60° - \theta)$, nor the projected area of the molecules on the surface, given by $\sin(60° - \theta)$, can explain the observed behavior. This shows that the increasing molecular interaction with increasing surface density must have affected the molecular orientation. The LE-LC transition, resulting from the molecular interaction and occurring at a definite surface density and molecular orientation, should be a transition for which both density and orientation come in as order parameters.

A question of continuing debate is whether or not the LE-LC transition is of first order and, consequently, whether there exists a region of coexisting phases in the π-A diagram. This can be answered by studying the local field effects of SHG[13] which we have neglected so far.

The incoming electric field of the incident pump beam will induce a dipole moment on each adsorbed molecule. When the molecules are close to each other, the induced dipole–induced dipole interaction will result in a change of the local fields at the molecules and, consequently, in a change in the SHG response.

If the local-field effect is taken into account, Eq. (2) should become

$$\chi_{zzz}^{(2)} = N_s L_z^3 \langle \cos^3\theta \rangle \alpha_{\xi\xi\xi}^{(2)},$$

$$\chi_{zzz} = N_s L_z L_x^2 \langle \sin^2\theta \cos\theta \rangle \alpha_{\xi\xi\xi}^{(2)}, \tag{3}$$

where the local field factors L_z and L_x will depend on the intermolecular distance d and their linear polarizability $\alpha^{(1)}$. Because of this d dependence, the local field factors are expected to be different for a homogeneous phase with all molecules having an averaged spacing d or for a coexistence phase with islands of closely packed molecules within a "lake" of farther separated liquid molecules. Using Ref. 13, we can make an estimate for L_z and L_x for both cases. The calculated χ_{zxx}/N_s vs A from Eq. (3) are plotted in Fig. 3 together with the experimental data. The results show that the assumption of a coexistence phase (dashed line) rather than of a homogeneous phase (dotted line) is definitely more correct. The dashed line was calculated for a coexistence region with the higher density domains having $A = 28$ Å^2/molecule and $\theta = 60°$ and the lower density phase having $A = 37$ Å^2/molecule and $\theta = 45°$. Our results here cannot distinguish whether the high-density domains are in the form of a liquid or a solid.[14] This question can only be answered definitely by structural data, but so far attempts to obtain these have not been successful.[15] Incidentally, we have found that in the present case, the local field factors do not change our molecular orienta-
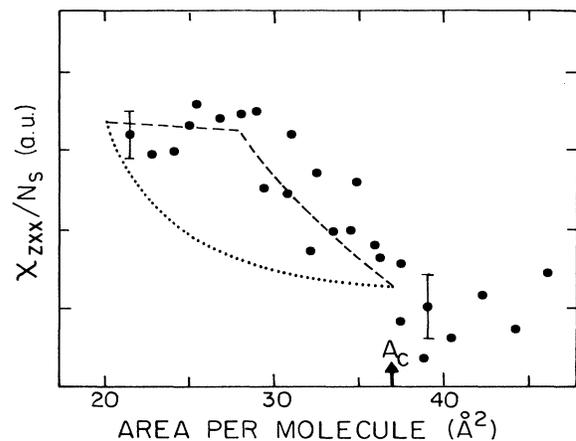
TABLE I. Tilt angle θ at the LE-LC transition point A_c for various temperatures.

T (°C)	A_c	θ
20.5	41	46
22	37	42
25	32	43
30	30	48

FIG. 3. χ_{zxx}/N_s as a function of the area per molecule for PDA on water at 22 °C. The dashed line is a calculation for a coexistence phase. The dotted line is a calculation for a homogeneous phase.

tion results by more than $\sim 6°$.

In conclusion, by use of the technique of optical SHG, we have been able for the first time to study the molecular orientation of a monolayer near the LE-LC phase transition. The results indicate that the observed transition is accompanied by an orientation of the molecules with the transition always taking place at roughly the same angle, independent of temperature. We also find strong evidence for the presence of a coexistence region between the LE and LC phases, indicating the first-order character of this transition. These results show that the LC phase is a higher-density phase with more orientational ordering.

---

[1]J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973); B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978); D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979).

[2]See, for instance, V. I. Imry, in *Chemistry and Physics of Solid Surfaces IV,* edited by R. Vanselow and R. Howe (Springer-Verlag, New York, 1982), p. 461, and references therein.

[3]M. W. Kim and D. S. Cannell, Phys. Rev. Lett. **35**, 889 (1975), and Phys. Rev. A **13**, 411 (1976).

[4]For a review, see, e.g., G. M. Bell, L. L. Coombs, and L. J. Dunne, Chem. Rev. **81**, 15 (1981).

[5]C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, Phys. Rev. Lett. **46**, 1010 (1981).

[6]T. F. Heinz, H. W. K. Tom, and Y. R. Shen, Phys. Rev. A **28**, 1883 (1983).

[7]H. W. K. Tom, T. F. Heinz, and Y. R. Shen, Phys. Rev. Lett. **51**, 1983 (1983).

[8]H. W. K. Tom, C. M. Mate, X. D. Zhu, J. E. Crowell, T. F. Heinz, G. A. Somorjai, and Y. R. Shen, Phys. Rev. Lett. **52**, 348 (1984).

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

[10]One can define an orientational order parameter as

$$Q = \frac{2\langle\cos^3\theta\rangle}{\langle\cos\theta\rangle} - 1 = \frac{\chi_{zzz}^{(2)} - 2\chi_{zxx}^{(2)}}{\chi_{zzz}^{(2)} + 2\chi_{zxx}^{(2)}},$$

with $Q = 0$ for random distribution and $Q = \pm 1$ for δ-function distributions at $\theta = 0$ and $\theta = \pi/2$, respectively.

[11]G. F. Graines, Jr., *Insoluble Monolayers at Liquid Gas Interfaces* (Wiley, New York, 1966).

[12]N. R. Pallas and B. A. Pethica, to be published.

[13]P. Ye and Y. R. Shen, Phys. Rev. B **28**, 4288 (1983).

[14]Recently, H. M. McConnell *et al.* [Proc. Natl. Acad. Sci. U.S.A. **81**, 3249 (1984)] have reported the observation of the formation of a domain lattice of a molecular monolayer at the LE-LC transition, but they only assume that the domains are in the solid phase. On the other hand, recent shear modulus data by B. M. Abraham *et al.* [Phys. Rev. Lett. **49**, 1643 (1982), and **51**, 1975 (1983)] indicate a much richer phase diagram than simply liquid-solid.

[15]S. Garoff, private communication.