

Orientational Fluctuations and Phase Transitions of Long Chain Molecules at the Air/Water Interface

Xiaolin Zhao, Suchitra Subrahmanyam, and Kenneth B. Eisenthal^(a)
Department of Chemistry, Columbia University, New York, New York 10027
 (Received 20 June 1991)

Orientational fluctuations in long chain molecules at the air/water interface were detected by second-harmonic spectroscopy. The fluctuations depend on the polarization of the incident (ω) and detected (2ω) light showing that the fluctuations are orientational rather than density in origin. The phenomenon is attributed to an orientational phase transition that is dependent on chain length, head group, and charge. Scaling experiments based on increasing the laser beam area indicated a correlation length (domain size) greater than $6 \mu\text{m}$ near the transition point.

PACS numbers: 68.10.-m

We wish to report the coverage-dependent orientational fluctuations of lipid molecules at the air/water interface, which we attribute to a heretofore unknown orientational phase transition. These lipid fluctuations were detected by the time-dependent variations (fluctuations) in the second-harmonic signal. They were shown to be orientational by the observations that the fluctuations depended on the polarization of the incident light field and that of the second-harmonic light field that was measured. The experimental results of this study bear on the organization of lipid molecules at the air/water interface, a subject that has been and remains one of intense experimental and theoretical activity [1]. A range of techniques has been used to study the various equilibrium phases and phase transitions of insoluble lipid monolayers. They include surface pressure, interface electric potential [2], light scattering [3], ellipsometry [4], fluorescence microscopy [5], x-ray and neutron diffraction, and reflection [6]. There have been a number of experimental and theoretical studies concerning orientational ordering [7] and orientational phase transitions [8]. However, it remains a difficult task to experimentally explore the relative importance of orientational and density ordering parameters,

especially since they can be coupled, in lipid phase transitions. The technique we have used in this research, second-harmonic generation (SHG) [9], is a relatively new technique sensitive to both the interface molecular density and molecular orientation. The surface sensitivity of SHG is a result of the fact that it is electric dipole forbidden in a centrosymmetric medium, such as a bulk liquid or gas, but allowed in the interfacial region where the symmetry is broken [10].

In this work we report on our studies of *p*-hexadecylaniline, $[\text{CH}_3-(\text{CH}_2)_{15}-\text{C}_6\text{H}_5\text{NH}_2]$, a long chain aniline where the aniline head group has C_{2v} symmetry. Neglecting local field effects the second-order susceptibility tensor $\chi^{(2)}$ can be related to the molecular nonlinear polarizability $\alpha^{(2)}$ by $\chi^{(2)} = N_s \langle \alpha^{(2)} \rangle$, where N_s is the lipid surface density (molecules/cm²) and the brackets refer to an average over molecular orientations. For an interface that is isotropic in the surface plane, i.e., is rotationally invariant with respect to the interface normal, populated by molecules of C_{2v} symmetry the explicit relation between $\chi^{(2)}$ and $\alpha^{(2)}$ yields the following expressions for two of the $\chi^{(2)}$ elements that we will be concerned with [11]:

$$\chi_{zxx}^{(2)} = \frac{1}{2} N_s [f(\alpha_{zzz}^{(2)}, \alpha_{zaa}^{(2)}, \alpha_{xza}^{(2)}, \theta, \psi) + \alpha_{zaa}^{(2)} \langle \cos\theta \rangle], \quad (1)$$

$$\chi_{xzx}^{(2)} = \frac{1}{2} N_s [f(\alpha_{zzz}^{(2)}, \alpha_{zaa}^{(2)}, \alpha_{xza}^{(2)}, \theta, \psi) + \alpha_{xza}^{(2)} \langle \cos\theta \rangle], \quad (2)$$

where

$$f(\alpha_{zzz}^{(2)}, \alpha_{zaa}^{(2)}, \alpha_{xza}^{(2)}, \theta, \psi) = \alpha_{zzz}^{(2)} \langle \cos\theta \sin^2\theta \rangle - (\alpha_{zaa}^{(2)} + 2\alpha_{xza}^{(2)}) \langle \cos\theta \sin^2\theta \sin^2\psi \rangle,$$

θ is the angle between the molecular symmetry axis \hat{z} and the surface normal z , and ψ is the rotation angle of the molecule about its symmetry axis \hat{z} . From Eqs. (1) and (2) we see that $\chi_{xzx}^{(2)}$ and $\chi_{zxx}^{(2)}$ differ only in the nonlinear polarizability coefficients of $\langle \cos\theta \rangle$, namely, α_{xza} and α_{zaa} .

The SH signal corresponding to these two elements, $\chi_{xzx}^{(2)}$ and $\chi_{zxx}^{(2)}$ [Eqs. (1) and (2)], were measured as a function of time using a synchronously pumped picosecond dye laser and a single-photon-counting detection system [12]. At sufficiently low lipid densities, e.g., greater than 38 \AA^2 , the system is in the liquid-gas coex-

istence region as seen in the surface pressure (π - A) phase diagram, Fig. 1. In this density region the fluctuations are density fluctuations and are therefore independent of the polarization of the incident light and that of the SH light measured; i.e., we find the fluctuations are the same for all of the $\chi^{(2)}$ elements [12].

On further compression to densities above 37 \AA^2 non-Poisson fluctuations were observed for $\chi_{xzx}^{(2)}$, Fig. 2(b). However, for $\chi_{zxx}^{(2)}$, the fluctuations observed were very close to a Poisson distribution, Fig. 2(a), thereby indicating that the fluctuations are due chiefly to photodetection

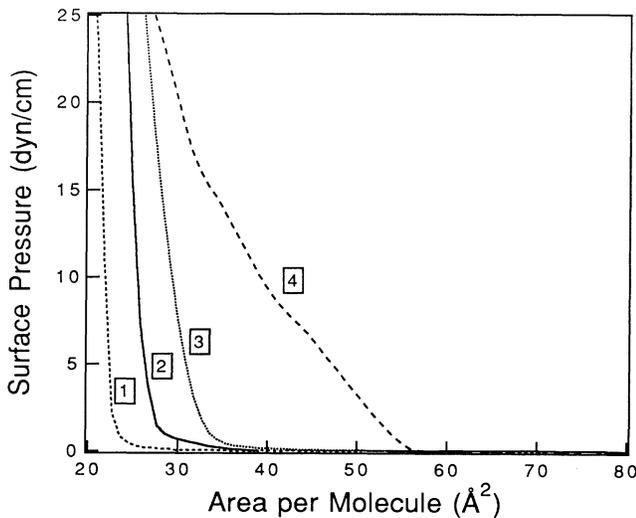


FIG. 1. Surface pressure (dyn/cm) vs area per molecule (\AA^2) isotherm on water or water solution subphase. Curve 1, C16 phenol over water; curve 2, C16 aniline over water; curve 3, C18 phenolate over $2N$ KOH; curve 4, C16 anilinium over $1N$ HCl.

noise and not due to molecular fluctuations at the interface. We therefore conclude that we are detecting a polarization-dependent and hence an orientational fluctuation. It should be noted that there is no indication from the π - A phase diagram, Fig. 1, of a phase transition in this density region of the liquid phase.

Further support that the observed fluctuations at densities $\geq 37 \text{\AA}^2$ are orientational was obtained from the simultaneous measurement of the s and p components of the SH signal for incident light polarized at 45° . This was achieved by using a polarizer to separate the s and p components of the SH light. Using C16 aniline at a surface coverage of 34\AA^2 , we found that the s -component fluctuations were much greater than those for the p -component. The large difference in the magnitude of s and p fluctuations results in a fluctuation of the polarization of the SH field, i.e., $\arctan(E_s^{2\omega}/E_p^{2\omega})$. From the magnitude of the fluctuations we estimate the fluctuation in polarization to be between 50° and 70° from the surface normal. It should be noted that the E_s component arises from the χ_{xzx} component whereas the E_p component arises from several of the susceptibility elements that cancel each other partially leading to a decrease in the magnitude of fluctuations. From the observed fluctuations in $\chi_{xzx}^{(2)}$ and the fluctuations in the polarization of the second-harmonic field we conclude that we are observing orientational fluctuations. On compressing the monolayer further we find that fluctuations decrease and at 28\AA^2 the fluctuations are approximately Poisson in character. We were unable to go to higher coverages because of the collapse of the monolayer below 28\AA^2 .

We now consider the basis for the orientational fluctua-

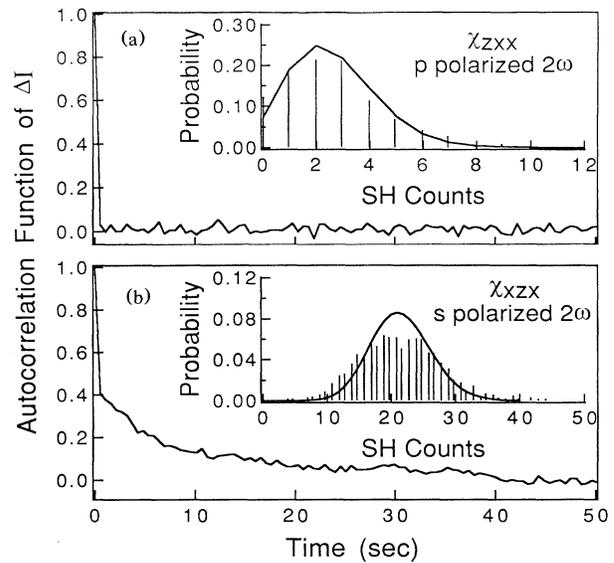


FIG. 2. Autocorrelation function of $\Delta I(t)$ and probability density function of SH signal counts of C16 aniline at 34\AA^2 : (a) with s -polarized input and p -polarized output corresponding to $\chi_{zxx}^{(2)}$; (b) with 45° -polarized input and s -polarized output corresponding to $\chi_{zzx}^{(2)}$.

tions. Since the SH signal is due chiefly to aniline, we note that the fluctuations that we observe must be due to the fluctuations in the orientation of the aniline head group. However, one cannot conclude from this that the driving force for these fluctuations is due only to head group interactions, e.g., via a dipole-dipole coupling between the head groups. It is quite reasonable that chain-chain interactions at these relatively high densities play some role in driving the head group orientational phase transition. We know that the chain-chain interactions cannot be the sole factor, however, since we do not observe any orientational fluctuations for an equal-chain-length lipid with a head group, having a similar dipole moment to aniline, namely, p -hexadecylphenol (n - $C_{16}H_{33}$ - C_6H_5OH).

Let us now consider the orientation of the aniline head group. Noting that the twist angle ψ is present only in the common function $f(a_{zga}^{(2)}, a_{gaa}^{(2)}, a_{zga}^{(2)}, \theta, \psi)$ for both $\chi_{xzx}^{(2)}$ and $\chi_{zxx}^{(2)}$, Eqs. (1) and (2) indicate that the $\langle \cos\theta \rangle$ term is responsible for the fluctuations, since it is only this term that differs for $\chi_{xzx}^{(2)}$ and $\chi_{zxx}^{(2)}$. In the common f term the θ dependence appears as $\langle \cos\theta \sin^2\theta \rangle$. Thus as θ fluctuates about some average value there would be a much smaller fluctuation in $\langle \cos\theta \sin^2\theta \rangle$ than in $\langle \cos\theta \rangle$ since as θ increases the $\cos\theta$ part would decrease and the $\sin^2\theta$ part would increase. From theoretical estimates $a_{zga}^{(2)}$ is much larger than $a_{gaa}^{(2)}$ for aniline [13]. This could result in $a_{zga}^{(2)} \langle \cos\theta \rangle$ being appreciable in $\chi_{xzx}^{(2)}$, whereas the $a_{gaa}^{(2)} \langle \cos\theta \rangle$ could be small relative to the f term in $\chi_{zxx}^{(2)}$. This would explain why we readily observed orientational

TABLE I. Correlation time τ_c (sec) dependence of area per molecule and observation spot size.

	36 Å ²	34 Å ²	32 Å ²	30 Å ²	28 Å ²
3 μm	9 ± 2	14 ± 2	16 ± 2	17 ± 3	< 15
6 μm	5 ± 2	6 ± 2	12 ± 3	17 ± 3	< 15

fluctuations in the $\chi_{zz}^{(2)}$ element and not in the $\chi_{zx}^{(2)}$ element.

In order to examine the spatial range of the orientational fluctuation we varied the laser beam area by a factor of 4 from a radius of 3 to 6 μm. The results of autocorrelation times for the two beam areas for various monolayer coverages are given in Table I. At 36 Å² there is a large decrease in the autocorrelation time for the larger beam radius. At 36 Å², which is away from the transition point (~30 Å²), the orientational domains would be expected to be smaller. As the laser spot size is increased the number of domains viewed increases, and therefore a more rapid decorrelation would be expected. As the transition point is approached the domains increase in size and the decay of the autocorrelation function would be slower, though still showing a change with spot size. This is seen to be the case at 36, 34, and 32 Å². At 30 Å² the system is near the transition point and the domains are very large, becoming larger than the beam size. This is seen in the result that the same decay time is observed for the 3- and 6-μm-radius beams, which indicates that the orientational correlation length is greater than 6 μm. If the transition were second order then this correlation length would diverge at the transition point. At the coverage of 28 Å² the fluctuations have decreased in magnitude to the extent that the distribution approaches Poisson and it is difficult in these initial experiments to extract a reliable autocorrelation decay time. We roughly estimate that the decay time is less than 15 sec for both beam radii. Based on the scaling experiments at the various coverages, which indicate a long correlation length, we infer that the phase transition is likely to be weak first order if not second order [14].

As alluded to earlier, the importance of chain-chain interactions on the observed orientational fluctuations is seen in the strong dependence of the SH fluctuations on the chain length of the aniline lipid. We find that the shorter-chain anilines have shorter correlation times and distributions closer to Poisson, thus indicating a more homogeneous surface on the time scale of our measurements. In fact, C12 aniline does not show any deviation from Poisson fluctuation for the experimental sampling time scale of 0.5 sec that we use. This could be due to a correlation length that is much smaller than the laser beam area (3-μm radius), and/or a relaxation that is much faster than the 0.5-sec sampling time. It is perhaps not surprising for the longer-chain anilines to effect a decrease in the orientational motion of the head group since

both packing and attractive interactions are stronger. However, the expected difference in chain-chain interactions is not reflected in the surface-pressure-area phase diagram for these various anilines; they are the same for the C12, C14, and C16 anilines.

To examine the effect of the head group on these orientational fluctuations we studied C14, C16, and C18 phenols. Although phenol and aniline have similar dipole moments, and the chain lengths were the same for both the aniline and phenol lipids, we observed no orientational fluctuations for any of the phenols. Perhaps the interactions of the head groups with the surrounding water molecules is an important factor, recognizing that the hydrogen-bonding properties of the aniline versus phenol are different [15].

A very interesting example of the necessary balance between the various forces, chain-chain, hydrogen-bonding, and electrostatic, involved in the orientational phase transition is our observation that the charged lipid C18-phenolate (C18-C₆H₅O⁻) manifests orientational fluctuations similar to the C16 aniline. The charged anilinium lipids (C16-C₆H₅NH₃⁺) and as noted earlier the neutral phenol lipids do not show orientational fluctuations.

In conclusion, unexpected fluctuations in the second-harmonic signal were observed in the monolayer liquid phase region of *p*-substituted long-chain anilines (C14 and C16) and C18 phenolate. The fluctuations depended on the polarization of the incident light and that of the second-harmonic light detected, as demonstrated by measuring different elements of the second-order susceptibility. It is inferred from these results that the signal fluctuations are due to fluctuations in the orientation of the head group rather than fluctuations in the density. This phenomenon is attributed to an orientational phase transition of the head group which strongly depends on interfacial interactions (monolayer-substrate, dipole-dipole or charge-charge, and chain-chain). Scaling experiments based on increasing the beam area by a factor of 4 showed that the decay time of the second-harmonic autocorrelation function was longer for the smaller laser beam area and that the correlation length (domain size) was greater than 6 μm near the transition point region (30 Å²). From these observations it was concluded that the phase transition is second order or weak first order.

We thank Professor Kenneth Dawson of the University of California, Berkeley, and Professor William Gelbart of the University of California, Los Angeles, and Professor Buyao Zhu of Peking University for helpful discussions and suggestions. We gratefully acknowledge support from the National Science Foundation and the Air Force Office for Scientific Research.

^(a)To whom correspondence should be addressed.

[1] G. L. Gaines, *Insoluble Monolayers at Liquid-Gas Interfaces* (Interscience, New York, 1966); C. M. Knobler, in

- Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Interscience, New York, 1990), Vol. 77, pp. 397-449.
- [2] N. R. Pallas and B. A. Pethica, *J. Chem. Soc. Faraday Trans. 1* **83**, 585 (1987); M. W. Kim and D. S. Cannell, *Phys. Rev. A* **13**, 411 (1976); **14**, 1299 (1976).
- [3] J. C. Earnshaw and P. J. Winch, *Thin Solid Films* **159**, 159 (1988); D. Langevin, *J. Colloid Interface Sci.* **80**, 412 (1981); H. Bercegol, F. Gallet, D. Langevin, and J. Meunier, *J. Phys. (Paris)* **50**, 2277 (1989).
- [4] Th. Rasing, H. Hsiung, Y. R. Shen, and M. W. Kim, *Phys. Rev. A* **37**, 2732 (1988).
- [5] B. Moore, C. M. Knobler, D. Braseta, and F. Rondelez, *J. Chem. Soc. Faraday Trans. 2* **82**, 1753 (1986); M. Losche and H. Mohwald, *Rev. Sci. Instrum.* **55**, 1968 (1984); H. M. McConnell, L. K. Tamm, and R. M. Weis, *Proc. Natl. Acad. Sci. U.S.A.* **31**, 3249 (1984); H. Mohwald, *Thin Solid Films* **159**, 1 (1988).
- [6] P. S. Pershan, *Faraday Discuss. Chem. Soc.* **89**, 231 (1990); K. Kjaer, J. Als-Nielsen, C. A. Helm, L. A. Laxhuber, and H. Mohwald, *Phys. Rev. Lett.* **58**, 2224 (1987); D. Vaknin, K. Kjaer, J. Als-Nielsen, and M. Losche, *Biophys. J.* **59**, 1326 (1991); B. Lin, J. B. Peng, J. B. Ketterson, P. Dutta, B. N. Thomas, J. Buontempo, and S. A. Rice, *J. Chem. Phys.* **90**, 2393 (1989); T. M. Bohanon, B. Lin, M. C. Shih, G. E. Ice, and P. Dutta, *Phys. Rev. B* **41**, 4846 (1990).
- [7] K. Kjaer, J. Als-Nielsen, C. A. Helm, L. A. Laxhuber, and H. Mohwald, *Phys. Rev. Lett.* **58**, 2224 (1987); S. Garoff, H. W. Deckman, J. H. Dunsmuir, M. S. Alvarez, and J. M. Bloch, *J. Phys. (Paris)* **47**, 701 (1986); C. A. Helm, H. Mohwald, K. Kjaer, and J. Als-Nielsen, *Biophys. J.* **52**, 381 (1987).
- [8] J. F. Baret, *Prog. Surf. Membr. Sci.* **14**, 291 (1981); G. M. Bell, J. Mingins, and J. A. G. Taylor, *J. Chem. Soc. Faraday Trans. 1* **74**, 223 (1978); Zhong-Ying Chen, J. Talbot, W. M. Gelbart, and A. Ben-Shaul, *Phys. Rev. Lett.* **61**, 1376 (1988); O. G. Mouristen and M. J. Zuckermann, *Chem. Phys. Lett.* **135**, 294 (1987); D. Andelman, F. Brochard, and J. Joanny, *J. Chem. Phys.* **86**, 3673 (1987); M. L. Mitchell and R. A. Dluhy, *J. Am. Chem. Soc.* **110**, 712 (1988); V. T. Moy, D. J. Keller, H. E. Gaub, and H. M. McConnell, *J. Phys. Chem.* **90**, 3198 (1986); V. T. Moy, D. J. Keller, and H. M. McConnell, *J. Phys. Chem.* **92**, 5233 (1988).
- [9] N. Bloembergen and P. S. Pershan, *Phys. Rev.* **128**, 606 (1962); C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, *Phys. Rev. Lett.* **46**, 146 (1981); *Chem. Phys. Lett.* **83**, 455 (1981); *Phys. Rev. B* **27**, 1965 (1983); J. M. Hicks, K. Kemnitz, K. B. Eisenthal, and T. F. Heinz, *J. Phys. Chem.* **90**, 560 (1986); K. Kemnitz, K. Bhattacharyya, G. R. Pinto, K. B. Eisenthal, and T. F. Heinz, *Chem. Phys. Lett.* **131**, 285 (1986); A. L. Harris, C. E. D. Chidsey, N. J. Levinos, and D. N. Loiacone, *Chem. Phys. Lett.* **141**, 350 (1987); G. Richmond, J. M. Robinson, and V. L. Shannon, *Prog. Surf. Sci.* **28**, 1-70 (1980).
- [10] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).
- [11] M. C. Goh, G. R. Pinto, K. Bhattacharyya, K. B. Eisenthal, and T. Heinz (to be published).
- [12] X. Zhao, M. C. Goh, S. Subrahmanyam, and K. B. Eisenthal, *J. Chem. Phys.* **94**, 3370 (1990).
- [13] M. Tichy and R. Zahradnik, *J. Phys. Chem.* **73**, 534 (1969); J. Zyss, *J. Chem. Phys.* **70**, 3333-3340 (1979).
- [14] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1980), 3rd ed., Pt. 1.
- [15] S. N. Vinogradov and R. H. Linnell, *Hydrogen Bonding* (Van Nostrand Reinhold, New York, 1971), Chap. 5, p. 122.