

Monolayer orientational fluctuations and a new phase transition at the air water interface detected by second harmonic generation

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Fluctuations in the second harmonic intensity were observed in a number of insoluble amphiphiles spread at an air/aqueous interface. The fluctuations, which depend on the polarization of both the incident light and the second harmonic light generated, indicate a new phase transition for which the orientation of the head group is the order parameter. It is found that the phase transition occurs in certain long chain aromatic species but not in others of the same chain length with different head groups. The phase transition is identified as a weak first order transition. Agreement is obtained with a modified Landau–Ginzburg equation in which the chain–chain interactions provide a friction for the motions of the head groups. © 1995 American Institute of Physics.

I. INTRODUCTION

Phase transitions in amphiphile insoluble monolayers have been of scientific interest for more than 50 years. A range of techniques including surface pressure, interface electric potential,¹ light scattering,² ellipsometry,³ fluorescence microscopy,⁴ x-ray and neutron diffraction and reflection⁵ have been used to study the various equilibrium phases and phase transitions of these quasi-two-dimensional systems. In a number of these experimental and theoretical studies, it has been proposed that the phase structure and phase transitions in an amphiphile monolayer could involve quantities such as density,¹ molecular configuration,⁶ and orientation,^{7–9} etc. as order parameters. However it remains a difficult task to experimentally explore the relative importance of orientational and density ordering parameters since they can be coupled together. In this study, the technique we use to obtain information on surface density and molecular orientation at the interface is the surface specific technique of second harmonic generation (SHG). For a general theory of SHG, the reader is referred to excellent treatments elsewhere.^{10–14}

In this paper studies of spontaneous orientation fluctuations in amphiphile monolayers that we attribute to a heretofore unknown orientational phase transition is presented. These amphiphile 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. In these experiments the SH signal is due to the dominating second order nonlinearity of the aromatic head group. Therefore the observed fluctuations in the SH signal are directly related to fluctuations in the orientation of the head group. Among the questions to be discussed are

- Are there spontaneous orientation fluctuations in the head group that produce the observed phase transition? or is it the tail?
- What is the origin of the spontaneous orientation fluctuation?

What are the roles of the dipole–dipole interactions, anisotropic dispersive interactions, hydrogen bonding, and electrostatic repulsion in such fluctuations?

- Can one model the dynamics of the fluctuation by modifying the Landau–Ginzburg theory?

II. BACKGROUND THEORY

A. Landau–Ginzburg free energy expansion

The hypothesis of the Landau–Ginzburg theory is that the free energy density function or rather the local value of the free energy can be expanded in terms of an order parameter $Q(\mathbf{r})$ and its spatial gradient $\nabla Q(\mathbf{r})$. This expansion is valid around but not too close to the critical point (Ginzburg criterion).¹⁵ In general, the free energy density function $F(Q, \nabla Q)$ takes the following form:

$$F(Q, \nabla Q) - F_0 = \frac{1}{2} \frac{\partial^2 F}{\partial Q^2} (\delta Q)^2 + \frac{1}{2} L (\nabla Q)^2, \quad (1)$$

where F_0 is the free energy density at the equilibrium state. The expansion is taken around the equilibrium state where by definition the first order derivative should vanish. L is introduced here to account for any energy cost due to an interface inhomogeneity ($\nabla Q \neq 0$).

The $Q(r)$ can be expanded in a Fourier series $\delta Q = Q(r) - Q_0 = \sum_k Q_k e^{i\mathbf{k}\cdot\mathbf{r}}$ which yield for the coefficient of $(\partial^2 F / \partial Q^2)_0$, $(\delta Q)^2 = \sum_k \sum_{k'} Q_k Q_{k'} e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}}$, and $(\nabla Q)^2 = -\sum_k \sum_{k'} \mathbf{k}\cdot\mathbf{k}' Q_k Q_{k'} e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}}$. Since we want the total free energy for the system we integrate the free energy density over the volume,

$$\begin{aligned} & \int d\mathbf{r} [F(Q, \nabla Q)] \\ &= \sum_k \sum_{k'} \left(\frac{1}{2} F_{QQ} - \frac{1}{2} L \mathbf{k}\cdot\mathbf{k}' \right) Q_k Q_{k'} \int d\mathbf{r} e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}} \\ &= \sum_{\mathbf{k}} \left(\frac{1}{2} F_{QQ} + \frac{1}{2} L k^2 \right) |Q_{\mathbf{k}}|^2. \end{aligned}$$

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The term $\frac{1}{2}Lk^2|Q_k|^2$ is the Fourier component that corresponds to the energy required for the system to deviate from a homogeneous interface. The interface at equilibrium has the possibility of being inhomogeneous and we assume can be characterized by a single mode k_0 . Since we are interested in the departures of the free energy from its equilibrium state we can use $k=k_0$ as the reference point for the deviation of the interface from its equilibrium value. We therefore use $\frac{1}{2}L(k-k_0)^2$ rather than $\frac{1}{2}Lk^2$. The final equation for the free energy is

$$F(Q, \nabla Q) - F_0 = \sum_k \left[\frac{1}{2} F_{QQ} + \frac{1}{2} L(k-k_0)^2 \right] |Q_k|^2, \quad (2)$$

where $F_{QQ} = (\partial^2 F / \partial Q^2)_{\text{eq}}$ by definition. $F(Q, \nabla Q) - F_0$ is the reversible work necessary for the system to move away from its equilibrium state. The form of this equation can also be obtained by writing the free energy in momentum space with respect to its minimum value and keeping only the quadratic term, i.e., making an harmonic approximation.¹⁶ Because the free energy density function has been expressed explicitly in terms of $|Q_k|$ in Eq. (2), we use $|Q_k|$ as the order parameter instead of $Q(\mathbf{r})$ in the following treatment.

The variable $|Q_k|^2$ appearing in the free energy equation is the Fourier component of the correlation function,

$$\langle Q(\mathbf{r}') Q(\mathbf{r}' + \mathbf{r}) \rangle_{\mathbf{r}'} = \sum_k |Q_k|^2 e^{i\mathbf{k}\mathbf{r}}.$$

The average value of $|Q_k|^2$, which we now refer to as $G_k = \langle |Q_k|^2 \rangle$ can be obtained by averaging over all possible configurations. The probability density of a given configuration is given by

$$w(|Q_k|) = \frac{\exp[-\beta \int (F - F_0) d\mathbf{r}]}{\int \exp[-\beta \int (F - F_0) d\mathbf{r}] d|Q_k|}.$$

This leads to

$$\langle |Q_k|^2 \rangle = G_k = \frac{k_B T}{V} \frac{1}{L(k-k_0)^2 + F_{QQ}}. \quad (3)$$

It should be noted that G_k is time independent and will be written in terms of an arbitrary time $t=0$ as $\langle |Q_k(0) Q_k(0)| \rangle$ at a later point in this discussion where the time dependent fluctuations are analyzed.

B. Correction to the Landau expansion near criticality

If $k_0=0$ and $F_{QQ}=0$, the system is said to be in a state of criticality because the spatial fluctuation is maximized around $k_0=0$, i.e., infinite wavelength. In such a state, the local order parameter $Q(r)$ will fluctuate greatly. In general, one states that at a critical point, the order parameter undergoes a huge spontaneous fluctuation. The huge fluctuations that occur when the critical state is approached make the quadratic expansion invalid, i.e. higher order terms must be considered. It is therefore necessary to include the higher order terms in the expansion. An estimate of this correction has been made using a diagrammatic expansion.¹⁶ It turns out however that the free energy density can still be expanded as

$$F(Q) - F_0 = \sum_k \left[\frac{1}{2} F_{QQ} + \frac{1}{2} L(k-k_0)^2 \right] |Q_k|^2, \quad (4)$$

where F_{QQ} contains these higher order corrections. In any case, when $F_{QQ}=0$, the point is regarded as the crossover point to instability, i.e., the system is unstable when $(\partial^2 F / \partial Q^2) < 0$.

C. Time dependent Landau–Ginzberg equation

Analogous to the dissipative (frictional) force equation which has the form $\eta \partial x / \partial t = -\partial V / \partial x$, the Landau–Ginzberg theory states that the order parameter of the system Q in the absence of an external field has the form,¹⁷

$$\frac{1}{\Gamma} \frac{\partial Q}{\partial t} = -\frac{\delta F}{\delta Q}. \quad (5)$$

The reciprocal of the Landau–Ginzberg damping constant Γ is analogous to the friction η .

The Landau–Ginzberg equation does not allow for thermal excitations, i.e., thermal fluctuations. It is these excitations however which are the origin of the stochastic processes in the monolayer phase transitions we are considering. To account for the thermal excitations, we add a random variable $A(\mathbf{k}, t)$ in momentum space and time in the Landau–Ginzberg equation, i.e., we will work with a Landau–Ginzberg stochastic equation,

$$\frac{1}{\Gamma} \frac{\partial |Q_k(t)|}{\partial t} = -\frac{\partial F}{\partial |Q_k(t)|} + A(\mathbf{k}, t). \quad (6)$$

It should be noted that the above equation has the same form as the Langevin equation used to describe dynamic phenomena in the presence of a potential and a stochastic force. Let us define the time dependent correlation function,

$$G_k(t) = \langle |Q_k(0)| |Q_k(t)| \rangle. \quad (7)$$

On multiplying both sides of Eq. (6) by $|Q_k(0)|$ and noting that $\langle |Q_k(0)| A(\mathbf{k}, t) \rangle = 0$ we obtain,

$$\frac{1}{\Gamma} \frac{\partial G_k(t)}{\partial t} = -F_{QQ} G_k(t) - L(k-k_0)^2 G_k(t). \quad (8)$$

The solution of this equation yields

$$G_k(t) = G_k(0) e^{-\Gamma[F_{QQ} + L(k-k_0)^2]t} \quad (9)$$

with $G_k(0) = \langle |Q_k|^2 \rangle = \langle |Q_k(0) Q_k(0)| \rangle$ which has the equilibrium value given by Eq. (3).

D. Theoretical analysis of the data

Let us suppose the laser light intensity has a Gaussian spatial distribution,

$$\frac{I(r)}{I_0} = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{r^2}{2\sigma^2}\right). \quad (10)$$

The second harmonic signal is proportional to I^2 . This means that the signal response calculation should include the weighting function,

$$f(\mathbf{r}) = \frac{1}{2\pi\sigma^2} \exp\left(-\frac{r^2}{\sigma^2}\right). \quad (11)$$

Let us consider first the fluctuation in the observation area. We will evaluate the signal fluctuation $\delta S(t)$ subject to $\delta Q(r, t)$, at time t ,

$$\delta S(t) = \int d\mathbf{r} f(r) \delta Q(\mathbf{r}, t). \quad (12)$$

It is easier to handle the above integral in momentum space. In two dimensions, $f(\mathbf{k})$ will take the following form:

$$f(\mathbf{k}) = \frac{1}{4\pi} \exp\left(-\frac{\sigma^2 k^2}{4}\right) = \frac{1}{4\pi} \exp\left(-\frac{k^2}{2k_L^2}\right) \quad (13)$$

with $k_L = (\sqrt{2}/\sigma)$.

$$\delta S(t) = \int d\mathbf{r} f(r) \delta Q(\mathbf{r}, t) = \int d\mathbf{r} f(r) \int d\mathbf{k} e^{i\mathbf{k}\mathbf{r}} Q_k(t).$$

Transforming to frequency space we obtain,

$$\delta S(t) = \int d\omega e^{i\omega t} \left[\int d\mathbf{r} f(r) \int d\mathbf{k} e^{i\mathbf{k}\mathbf{r}} Q_k(\omega) \right]. \quad (14)$$

Therefore,

$$\begin{aligned} \delta S(\omega) &= \int d\mathbf{r} f(r) \int d\mathbf{k} e^{i\mathbf{k}\mathbf{r}} Q_k(\omega) \\ &= \int d\mathbf{k} Q_k(\omega) \int d\mathbf{r} e^{i\mathbf{k}\mathbf{r}} f(r) = \int d\mathbf{k} Q_k(\omega) f(k). \end{aligned} \quad (15)$$

With $Q_k(\omega) = |Q_k(\omega)| e^{i\phi(k, \omega)}$. The $\phi(k, \omega)$ is a random variable due to the stochastic properties of the fluctuation. Because of this random phase, only those elements with the same phase will be added constructively, i.e., only $f(k_1) f(k_2) Q_{k_1}(\omega) Q_{k_2}^*(\omega) \delta(\mathbf{k}_1 - \mathbf{k}_2)$, in the calculation of $\delta S(\omega) \delta S^*(\omega)$. Therefore, we obtain

$$\delta S(\omega) \delta S^*(\omega) = 2\pi \int k dk [f(k)]^2 |Q_k(\omega)|^2. \quad (16)$$

To obtain $|Q_k(\omega)|^2$ we Fourier transform Eq. (9),

$$|Q_k(\omega)|^2 = \frac{k_B T}{V} \frac{\Gamma}{\omega^2 + \Gamma^2 [F_{QQ} + L(k - k_0)^2]^2} \quad (17)$$

and the final result of $S(\omega)$ is

$$\begin{aligned} \delta S(\omega) \delta S^*(\omega) &= \frac{2\pi \Gamma k_B T}{V} \\ &\times \int k dk \frac{[f(k)]^2}{\omega^2 + \Gamma^2 [F_{QQ} + L(k - k_0)^2]^2}. \end{aligned} \quad (18)$$

The autocorrelation function $\langle \delta S(0) \delta S(t) \rangle$ simply goes as

$$\begin{aligned} \langle \delta S(0) \delta S(t) \rangle &= \int d\omega e^{i\omega t} \delta S(\omega) \delta S^*(\omega) \\ &= \frac{2\pi k_B T}{V} e^{-\Gamma F_{QQ} t} \\ &\times \int k dk \frac{[f(k)]^2}{F_{QQ} + L(k - k_0)^2} e^{-\Gamma L t (k - k_0)^2}. \end{aligned} \quad (19)$$

The normalized autocorrelation function is

$$\frac{\langle \delta S(0) \delta S(t) \rangle}{\langle \delta S(0) \delta S(0) \rangle} = e^{-\Gamma F_{QQ} t} \frac{\int k dk \frac{[f(k)]^2}{F_{QQ} + L(k - k_0)^2} e^{-\Gamma L t (k - k_0)^2}}{\int k dk \frac{[f(k)]^2}{F_{QQ} + L(k - k_0)^2}}. \quad (20)$$

In terms of numerical fitting, there will be three fitting parameters (a) k_0 , (b) ΓL , (c) ΓF_{QQ} or (F_{QQ}/L) . In our experiment, we will use these parameters to fit the autocorrelation function of C16 aniline at four different surface coverages and for three different chain length anilines.

III. AMPHILPHILE SYSTEM AND SHG

In this work we report on our studies of a series of long chain para substituted amphiphiles having as the head group one of the following: aniline, $C_6H_4NH_2$; phenol, C_6H_4OH ; anilinium, $C_6H_4NH_3^+$; phenolate, $C_6H_4O^-$; N,N-dimethyl aniline, $C_6H_4N(CH_3)_2$; and trimethyl anilinium, $C_6H_4N^+(CH_3)_3$. Neglecting local field effects the second order susceptibility tensor $\chi^{(2)}$ can be related to the molecular nonlinear polarizability $\alpha^{(2)}$ by $\chi^{(2)} = N_s \langle \alpha^{(2)} \rangle$. For an interface that is isotropic in the surface plane, i.e., is rotationally invariant with respect to the interface normal, two of the $\chi^{(2)}$ elements that we will be concerned with can be written as,⁹

$$\chi_{zxx}^{(2)} = \frac{1}{2} N_s \{ f[\alpha_{zzz}^{(2)}, \alpha_{zxx}^{(2)}, \alpha_{xzxx}^{(2)}, \theta, \psi] + \alpha_{zxx}^{(2)} \langle \cos \theta \rangle \}, \quad (21)$$

$$\chi_{xzx}^{(2)} = \frac{1}{2} N_s \{ f[\alpha_{zzz}^{(2)}, \alpha_{zxx}^{(2)}, \alpha_{xzxx}^{(2)}, \theta, \psi] + \alpha_{xzx}^{(2)} \langle \cos \theta \rangle \}, \quad (22)$$

where N_s is the surface density, and

$$\begin{aligned} f[\alpha_{zzz}^{(2)}, \alpha_{zxx}^{(2)}, \alpha_{xzxx}^{(2)}, \theta, \psi] \\ = \alpha_{zzz}^{(2)} \langle \cos \theta \sin^2 \theta \rangle - [\alpha_{zxx}^{(2)} + 2\alpha_{xzxx}^{(2)}] \\ \times \langle \cos \theta \sin^2 \theta \sin^2 \psi \rangle, \end{aligned}$$

θ is the angle between the molecular symmetry axis z and the surface normal Z , and ψ is the rotation angle of the molecule about its symmetry axis z . From Eqs. (21) and (22) we see that $\chi_{zxx}^{(2)}$ and $\chi_{xzx}^{(2)}$ differ only in the nonlinear polarizability coefficients of $\langle \cos \theta \rangle$, namely $\alpha_{zxx}^{(2)}$ and $\alpha_{xzx}^{(2)}$.

IV. EXPERIMENT

All long chain anilines were purchased from Aldrich (97% purity) and were further purified by recrystallization from ethanol. All long chain phenols were synthesized by standard methods and purified by recrystallization from hexane and ethanol. C16 N,N-dimethyl aniline, $\text{CH}_3(\text{CH}_2)_{15}\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$, and C16 N,N,N-trimethyl anilinium iodate salt, $\text{CH}_3(\text{CH}_2)_{15}\text{C}_6\text{H}_4\text{N}^+(\text{CH}_3)_3\text{IO}_3^-$ were synthesized from C16 aniline by refluxing with CH_3I in ethanol solution. The reactants mixture passing through silica gel column were separated into three components. The components corresponding to C16 N,N-dimethyl aniline and C16 N,N,N-trimethyl anilinium iodate salt were identified by NMR and mass spectrum. The raw products were further purified by recrystallization from ethanol.

The SH signal corresponding to the two elements, $\chi_{xz}^{(2)}$ and $\chi_{zzx}^{(2)}$ [Eqs. (21) and (22)], were measured as a function of time using a synchronously pumped picosecond dye laser and a single photon counting detection system.⁹

To simultaneously measure the p and s polarized components of the SH signal, the collected SH light was first collimated and passed through a pair of polarizer cubes. The first cube passes the E_p component of the SH light and reflects the E_s component out the side window. The E_s component was time delayed by 5 ns and then recombined with the E_p at the second cube. Both E_s and E_p then passed through a monochromator and were detected by the single photon counting system. The 5 ns time separation between E_s and E_p allowed the simultaneous measurement of both elements using the same photomultiplier tube and time correlated single photon counting system. The Π -A phase diagrams were measured using the Wilhelmy plate method.

V. RESULTS

The experiments reported were carried out at densities corresponding to the condensed phase region of the monolayer. For the long chain anilines, from C12 to C16, the phase diagrams are essentially the same, all having the gas-liquid phase coexistence boundary at 37 \AA^2 . For long chain phenols, from C14 to C18, the phase diagrams are also the same, and the monolayer gas-liquid phase coexistence end at 27 \AA^2 . This insensitivity of phase diagram to the chain length indicates that the LE-LC phase transition for each series should occur at a much shorter chain length. Therefore the chain configuration phase transition is not encountered in our studies.

A. The samples showing orientational fluctuation

We observed orientational fluctuations in four samples, the C16 and C14 anilines, C18 phenolate, and C16 N,N-dimethyl aniline. None of the phase diagram show any clear plateau or kinks in the density region where the orientational fluctuations are observed (Fig. 1). One thing that these samples have in common is that they are electron rich species, which allows for a large anisotropic dispersive interaction between the aromatic chromophores.

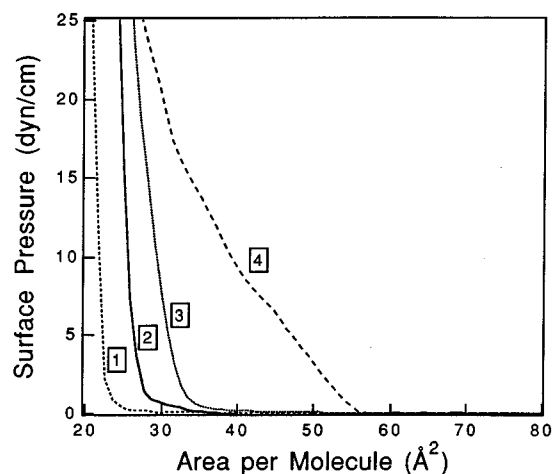


FIG. 1. Surface pressure vs area per molecule isotherm on water or water solution subphase. Curve 1, C16 phenol over water; curve 2, C16 aniline over water; curve 3, C18 phenolate over 2N KOH; curve 4, C16 anilinium over 1N HCl.

1. The orientation fluctuation for C16 aniline/water

The liquid phase of C16 aniline starts at 37 \AA^2 . At this density, the SH fluctuations obey Poisson statistics and the time autocorrelation function of the SH signal fluctuation is close to a δ -function, which indicates a homogeneous surface. This is consistent with the Π -A phase diagram which shows that the coexistence region has ended and the monolayer is a single phase liquid region. On further compression to densities above 37 \AA^2 non-Poisson fluctuations were observed for $\chi_{xz}^{(2)}$ [Fig. 2(b)]. However, for $\chi_{zzx}^{(2)}$, the fluctuations observed were very close to a Poisson distribution [Fig. 2(a)]. This indicates that the fluctuations are due chiefly to photodetection noise and not due to molecular fluctuations at the interface. We therefore conclude that we are detecting a polarization dependent fluctuation 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 $A \leq 37 \text{ \AA}^2$ are orientational was obtained from the simultaneous measurement of the E_s and E_p components of the SH signal for incident light polarized at 45° . Using C16 aniline at a surface coverage of 34 \AA^2 , we found that the s component fluctuations were much greater than that 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 find that the polarization fluctuates between the angles of 50° and 75° with respect to the surface normal. It should be noted that the E_s component arises from the $\chi_{xz}^{(2)}$ component whereas the E_p component arises from several susceptibility elements. These various elements have opposite signs due to their Fresnel coefficients which decrease the magnitude of the fluctuations. From the observed fluctuations in $\chi_{xz}^{(2)}$ and the fluctuations in the polarization of the second harmonic field we conclude that we are observing orientational fluctuations. On compressing the monolayer

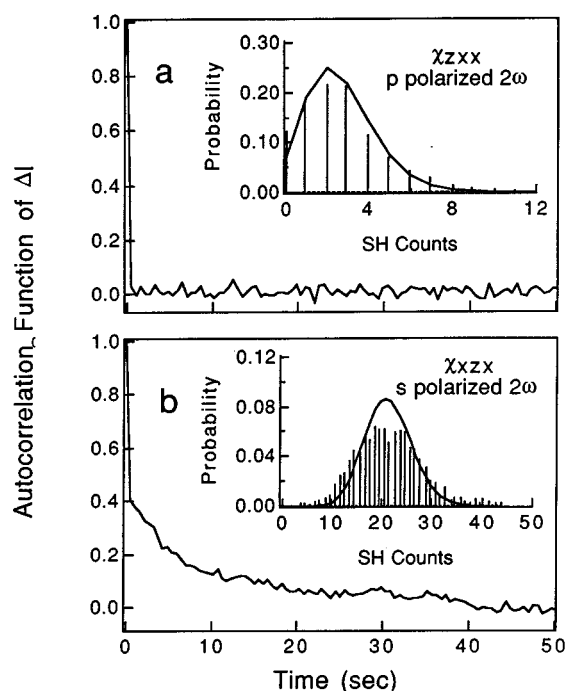


FIG. 2. Autocorrelation function of $\Delta I(t)$ and probability density function of SH signal counts of C16 aniline at 34 \AA^2 (a) with s polarized input and p polarized output corresponding to $\chi_{zzx}^{(2)}$, (b) with 45° polarized input and s polarized output corresponding to $\chi_{zzx}^{(2)}$.

further we find that fluctuations maximize in amplitude and correlation time at around 30 \AA^2 . They then sharply decrease at 28 \AA^2 where the fluctuations become approximately Poisson in character (Fig. 3). We were unable to go to higher coverages because the monolayer collapses below 28 \AA^2 .

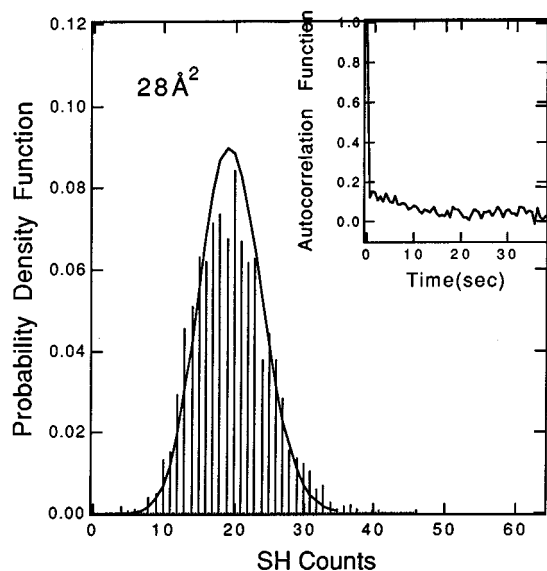


FIG. 3. The autocorrelation function and probability density function of C16 aniline monolayer at the surface coverage of 28 \AA^2 .

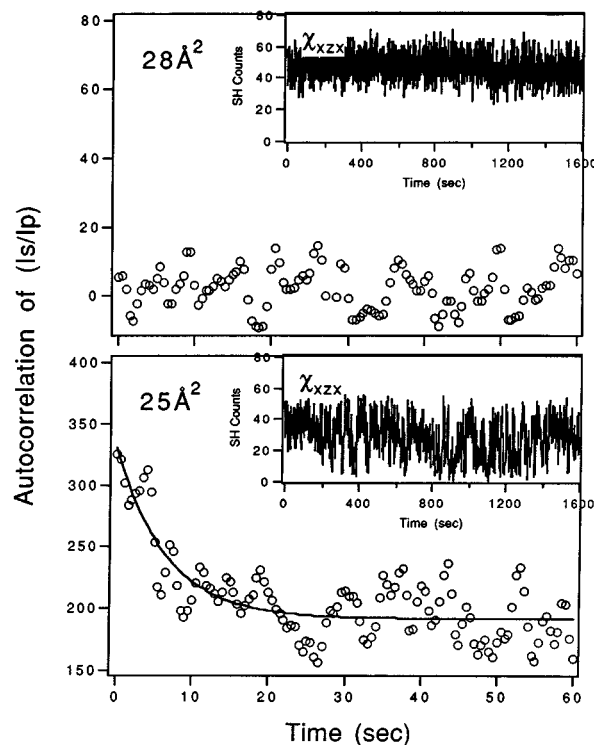


FIG. 4. The autocorrelation function of the ratio of (I_p/I_s) of N,N-dimethyl-C16-aniline, $\text{CH}_3(\text{CH}_2)_{15}\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2/\text{water}$ monolayer at 28 and 25 \AA^2 . The I_p and I_s components were simultaneously measured as described in the context.

The observed change in the polarization of the second harmonic light by 10° on going from the low density side of the transition to the high density side indicates that the phase transition is a structural change corresponding to a change in the tilt angle of the amphiphile head group.

2. The orientational fluctuation for C18 phenolate

The pK_a of phenol at the air/water interface is 11.7.¹⁸ Using this value the phenol monolayer should be completely ionized to C18 phenolate at 2N KOH, which corresponds as expected to the constant maximum value observed in the SH signal at this and higher pH values.

Once again in this monolayer we observed that $\chi_{zzx}^{(2)}$ shows large fluctuations whereas the $\chi_{zzx}^{(2)}$ element does not. This once again indicates the orientational origin of the signal fluctuation. The signal fluctuation peaks at $34\text{--}32 \text{ \AA}^2$ and then rapidly decreases showing no large fluctuations at a coverage of 30 \AA^2 .

3. The orientational fluctuation for N,N-dimethyl C16 aniline/water

The condensed phase of N,N-dimethyl C16 aniline, $\text{CH}_3(\text{CH}_2)_{15}\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$, starts at 28 \AA^2 . Upon further compression, the fluctuation magnitude increases and reaches a maximum at 25 \AA^2 , after which they decrease sharply to the random noise level (Fig. 4). To examine the origin of the SH fluctuation, E_s and E_p were simultaneously measured. The autocorrelation functions of (I_s/I_p) at 28 \AA^2

and 22 \AA^2 show a δ -function decay that is expected from fluctuations due to photon counting statistics indicating that we are at densities outside the phase transition region. At 25 \AA^2 however there is a distinct slow time decay observed as shown in Fig. 4. These fluctuations in the polarization of the SH light strongly support the orientation origin of the SH fluctuation.

It should be noted that the difference between C16 aniline and C16-N,N-dimethyl aniline is their hydrogen bonding ability with water. This suggests that hydrogen bonding, though very important in molecular orientation, is not the deciding parameter in the observed orientational fluctuations.

B. The amphiphiles showing no orientational fluctuation

We also measured the SH signals from the C14 phenol, C16 phenol, C18 phenol, C16 anilinium, C18 pyridinium bromide, $\text{CH}_3(\text{CH}_2)_{17}\text{C}_5\text{H}_4\text{NH}^+\text{Br}^-$; C22 pyridinium bromide, $\text{CH}_3(\text{CH}_2)_{21}\text{C}_5\text{H}_4\text{NH}^+\text{Br}^-$; and C16-N,N,N-trimethyl anilinium, $\text{CH}_3(\text{CH}_2)_{15}\text{C}_6\text{H}_4\text{N}^+(\text{CH}_3)_3$. None of these samples showed any fluctuations beyond the Poisson distributed noise fluctuations due to the single photon counting detection.

C. Dependence of orientational fluctuations on chain length

The importance of chain-chain interactions on the observed orientational fluctuations is seen in the strong dependence of the decay of the SH fluctuations on the chain length of the aniline amphiphile (Fig. 5). We find that the shorter the chain length of the aniline, the shorter is the correlation time, and the closer is the statistics to a Poisson distribution. This indicates that the monolayer surfaces for the short chain anilines are more homogeneous on the time scale of our measurements than the C16 aniline. In fact the probability density function of the SH signal from C12-aniline does not show any deviation from Poisson fluctuation for the experimental sampling time scale of 0.5 s that we use. This could be due to a correlation length for the C12-aniline that is much smaller than the laser beam area ($3 \mu \text{ radii}$), and/or a relaxation that is much faster than the 0.5 s sampling time. It is perhaps not surprising that the orientational motions of the head group are slower for the longer chain anilines since both packing and attractive interactions are stronger.

VI. ORDER PARAMETER: NATURE OF THE ORIENTATIONAL PHASE TRANSITION

We now consider the basis for the orientational fluctuations. As noted earlier, we observed for a number of amphiphiles, the appearance of orientational fluctuations whose magnitude and decay time depended on the monolayer surface density. We observed that as surface density increases, the fluctuation magnitude and time scale start to increase, then reach a maximum, and finally decrease to the normal random noise level associated with photon counting statis-

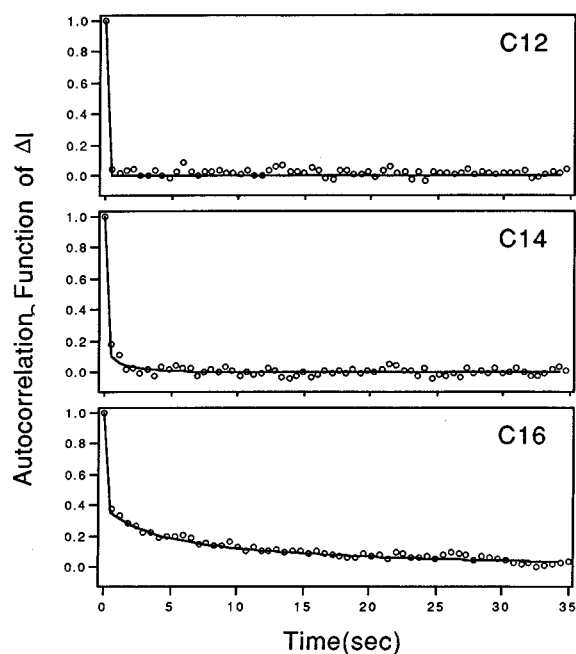


FIG. 5. Comparison of calculations and data at different chain lengths. The numerical calculation of the autocorrelation function of ΔI at 34 \AA^2 of C12, C14, and C16 aniline assuming the linear free energy relationship of the damping constant Γ with 700 cal/mol for each methylene group. Solid lines are calculations and circles are data points.

tics. As the surface density increases, the monolayer evolve from one phase state to another with molecular orientation as the order parameter.

Since the SH signal is due chiefly to the aromatic head group we note that the fluctuations that we observe must be due to the fluctuations in the orientation of the head group. However one cannot conclude from this that the driving force for these fluctuations are due only to head group interactions, e.g., via a dipole-dipole or dispersive couplings between the head groups. It is quite reasonable that chain-chain interactions at these relatively high densities play some role in the head group orientational phase transition. We know that the chain-chain interactions cannot be the major factor however since we do not observe any orientational fluctuations for an equal chain length amphiphile with a head group, having a similar dipole moment to aniline, e.g., *p*-hexadecylphenol, $n\text{-CH}_3(\text{CH}_2)_{15}\text{-C}_6\text{H}_4\text{OH}$.

Let us now consider the orientation of the aniline head group. Noting that the twist angle ψ is present only in the common function $f[\alpha_{zzz}^{(2)}, \alpha_{zxx}^{(2)}, \alpha_{xzx}^{(2)}, \theta, \psi]$ for both $\chi_{xzx}^{(2)}$ and $\chi_{zxx}^{(2)}$, Eqs. (21) and (22) 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 term f appearing in Eqs. (21) and (22), the θ dependence is contained in $\langle \cos \theta \sin^2 \theta \rangle$. 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 changes $\cos \theta$ and $\sin^2 \theta$ move in opposite directions, thereby reducing any net change in $\langle \cos \theta \sin^2 \theta \rangle$. From theoretical estimates $\alpha_{xzx}^{(2)}$ is much larger than $\alpha_{zxx}^{(2)}$ for aniline.¹⁹ This could result in $\alpha_{xzx}^{(2)} \langle \cos \theta \rangle$ being appreciable

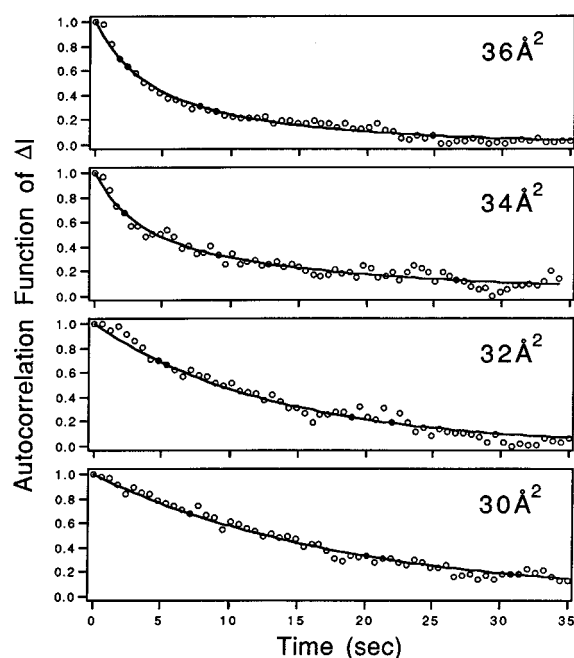


FIG. 6. The numerical fitting of the autocorrelation function of ΔI to the Landau-Ginzburg theory at 36, 34, 32, 30 \AA^2 of C16 aniline.

in $\chi_{zxz}^{(2)}$, whereas the $\alpha_{zxx}^{(2)}\langle\cos\theta\rangle$ could be small relative to the f term in $\chi_{zxx}^{(2)}$. This would explain why we readily observed orientational fluctuations in the $\chi_{zxz}^{(2)}$ element and not in the $\chi_{zxx}^{(2)}$ element for C16 aniline, C18 phenolate and N,N-dimethyl C₁₆-aniline.

The order parameter must be an observable quantity which changes its value during the phase transition. The above discussion in fact suggests that the order parameter is related to $\cos\theta$. This hypothesis is justified for the following reasons: (a) the only difference in χ_{zxz} and χ_{zxx} is the $\langle\cos\theta\rangle$ term; (b) $\cos\theta$ used as the order parameter is consistent with the observation that the molecule has some preferential orientation at the interface which can be described by the orientation of its dipole moment; (c) the fluctuation of $\cos\theta$ goes through a maximum as surface density increases, which is typical order parameter behavior during a phase transition.

Spatial extent of fluctuation

In order to examine the spatial range of the orientational fluctuations we varied the laser beam area by a factor of 4 from a radius of 3–6 μm . If the SH fluctuation is due to the translational motion of domains with different orientation order, one would expect that a domain would take a longer time to move across the larger laser beam; therefore a longer correlation time would be expected. For C16 aniline, it is found that at any surface coverage, the correlation time for a larger laser beam is less than or equal to that for a smaller laser beam (Table I). This observation strongly suggests that the orientation fluctuation we observed is not due to the translational motion of domains, but rather is due to spontaneous long range orientation fluctuations of the head group.

We now consider the origin of the dependence of the autocorrelation decay time on beam size. At 36 \AA^2 the

TABLE I. Correlation time τ_c (s) as a function of area per molecule and laser radius at interface.

	Area/molecule (\AA^2)				
	36 \AA^2	34 \AA^2	32 \AA^2	30 \AA^2	28 \AA^2
3 μm	9 \pm 2	14 \pm 2	16 \pm 2	17 \pm 3	<15
6 μm	5 \pm 2	6 \pm 2	12 \pm 3	17 \pm 3	<15

smaller autocorrelation time for the larger beam radius can be understood in terms of the relative sizes of the correlation length (domain size) to the laser spot size. At a density of 36 \AA^2 the interface is well away from the transition point (\sim 30 \AA^2) and consequently the orientational correlation length is expected to be significantly smaller than the beam radius of 6 μm . Because the domain size is much less than the laser beam area the number of domains within the laser spot is greater for the larger beam than for the smaller beam. These different domains are independent and decorrelate more rapidly as their number increases, thereby yielding a more rapid autocorrelation decay. 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 \AA^2 , 34 \AA^2 , and 32 \AA^2 . At 30 \AA^2 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 μm and 6 μm radii beam (Table I), from which we infer that the orientational correlation length is greater than 6 μm . It should be noted that the laser beam has a Gaussian spatial profile and most of the SH signal comes from a smaller radius than $\langle\sigma\rangle=6\mu$. If the transition was truly second order then this correlation length would diverge at the transition point. At the coverage of 28 \AA^2 the fluctuations have decreased in magnitude and the distribution approaches Poisson and it is difficult to extract a reliable autocorrelation decay time for these small fluctuations. We roughly estimate that the decay time is less than 15 s 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 a weak first order transition.

VII. CHAIN LENGTH DEPENDENCE OF AUTOCORRELATION DECAY: THEORY AND EXPERIMENT

There are three fitting parameters in the numerical fitting, i.e., k_0 , (F_{QQ}/L) , and ΓL . The data of C16 aniline at 36, 34, 32, 30 \AA^2 have been fitted to Eq. (20). The fitting

TABLE II. Results of the numerical fitting to the Landau-Ginzburg model.

	36 \AA^2	34 \AA^2	32 \AA^2	30 \AA^2
k_0 (10^4 cm^{-1})	2.05	2.05	1.68	1.38
$\frac{F_{QQ}}{L}$ (10^7)	2.41	1.16	46.0	54.3
ΓL (10^{-9})	1.83	2.26	0.142	0.093

results for C16 aniline are presented in Fig. 6. The fitting parameter value of each fit is presented in Table II.

Let us first look at k_0 . From 36 to 30 \AA^2 , k_0 decreases from 20 000 to 13 000 cm^{-1} indicating that wavelength at the interface is increasing $\lambda = (2\pi/k_0) = 3\text{--}5 \mu\text{m}$. This wavelength is comparable to our focus size. The value of (F_{QQ}/L) in general increases by one order of magnitude with a minimum at 34 \AA^2 while the value of ΓL decreases by two orders of magnitude monotonically. This trend could be due in part to the monotonical decrease of L as well as a decrease of Γ . A decrease in L means that there is less energy cost to move the system from its equilibrium state, i.e., the fluctuation is much easier to excite. Another view of the decreasing L is that the system is moving towards certain criticality. The nonzero k_0 and a decreasing L is in fact consistent with a weak first order phase transition picture.

Let us now re-examine the chain length dependence of the fluctuation. Chain-chain interactions can act as a frictional force on the head group motion. As the chain gets longer, it is expected that the friction or drag on the head group motion will increase. In the Landau-Ginzburg equation, the friction or drag is presented in the damping constant Γ . Assuming that the orientation spontaneous fluctuation results only from the head group interaction and that the chain-chain interaction provides the friction for the head group motion, we propose that for the same head group, the k_0, F_{QQ}, L will be the same at the same surface coverage and that the difference in the chain-chain interaction appears in Γ only. Under these assumptions, the value of Γ should follow the linear free energy relationship which states that for a homologous organic compound, the total free energy shall depend linearly on the chain length, i.e., the free energy contribution from each CH_2 is a constant. Therefore we should check the validity of the proposal that the observed orientation fluctuation results only from the head group interaction by examining the chain length dependence of Γ . Let us assume that $\Gamma = \Gamma_0 \exp(n\Delta E/kT)$, where n is the chain length, and ΔE is the free energy contribution from each methylene group. We found that when $\Delta E = 700$ cal/mol/methylene group, using the value obtained from C16 aniline data, we can actually predict the autocorrelation function of C14 and C12 aniline as shown in Fig. 5. This free energy value per methylene group is in the same range (700–800 cal/mol/methylene group) obtained from the free energy of the formation of hydrocarbon micelles and for the adsorption of hydrocarbon surfactant to the air/water interface.^{20,21} This value contains the contribution of the chain-chain interactions to the micelle formation and surface adsorption. The excellent fitting shown in Fig. 5 strongly supports the assumption that our observed orientational spontaneous fluctuation can be treated by a Landau-Ginzburg-type theory with the chain-chain interactions acting as the damping force.

VIII. CONCLUSIONS

Unexpected fluctuations in the second harmonic signal were observed in the monolayer liquid phase region of *p*-substituted C14, C16 aniline, C16 N,N-dimethyl aniline, and C18 phenolate. The fluctuations depended on the polar-

ization of the incident light and that of the second harmonic light generated. This was demonstrated in two different ways. One was by measuring different elements of the second order susceptibility and the second by the simultaneous measurement of the E_s and E_p components of the SH light. It is inferred from these results that

- We observe a new phase transition in the monolayer with the orientation of the head group as the order parameter. The strong fluctuation and nonzero k_0 , where k_0 is a measure of the extent of the spatial fluctuation at the interface, indicates that the phase transition is weakly first order.
- The phase transition occurs only in certain long chain aromatic species indicating that the interactions between the head groups is the controlling factor.
- The observed change in the polarization of the second harmonic light on going from the low density side of the transition to the high density side indicates that the phase transition is a structural change corresponding to a change in the tilt angle of the amphiphile head group.
- The chain-chain interactions provide a frictional force which exerts a drag on the motion of the head group. These interactions set the time scale of the head group dynamics.
- Scaling experiments based on increasing the beam area by a factor of 4 showed that the correlation length at the transition region was greater than 6 μm for C16 aniline.
- The fluctuation dynamics as a function of chain length and amphiphile density are in excellent agreement with a modified Landau-Ginzburg theory of the phase transition.

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