PHYSICAL REVIEW E **66**, 061605 (2002)

Monolayers at the air-water interface: Maxwell displacement current and optical second-harmonic generation studies and theoretical treatment

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(Received 28 August 2002; published 16 December 2002)

The structural properties and the surface pressure π-A isothermal diagram have been investigated during compression of the 4-n-pentyl-4$'$-cyanobiphenyl (5CB) monolayer film on the water surface, both experimentally, using both the Maxwell displacement current (MDC) and optical second-harmonic generation (SHG) techniques, and theoretically, in the framework of the molecular model, assuming that the randomly tilted polar 5CB molecules on the water surface are replaced by the collective tilted array of unit vectors. The average angle is evaluated based on the both MDC and SHG techniques. The reasonable agreement between the calculated and experimental values of $\pi(A)$ was obtained.

DOI: 10.1103/PhysRevE.66.061605 PACS number(s): 68.03.−g, 68.15.+e, 61.30.Cz, 66.20.+d

I. INTRODUCTION

The problem of predicting physical properties of monolayer films based upon information on molecular shape and intermolecular interactions remains one of the most fundamental problems in Langmuir monolayers physics [1–3]. For the physicist, monolayers of surfactants at the air-water interface provide an interesting two-dimensional (2D) system with very rich phase behavior [3]. Typically, as a film is compressed, it passes from a gas phase to a more condensed liquid phase, and then, sometimes, into a solid phase before finally becoming a monolayer film. The existence of transitions between the different phases is most commonly determined from surface pressure (π) - area (A) isotherm measurements [1,2,4]. Molecules in liquid crystal (LC) phases of Langmuir films either align normal to the air-water interface or they can tilt relative to the interface, thereby defining an array of a unit vectors $\mathbf{u}_i$ in the plane of the film [3]. Taking into account the state of the monolayer composed of, for example, rodlike polar molecules, characterized by a set of distribution functions depending on the heads molecules positions on the water surface and the hydrophobic ''tail'' orientations of the polar molecules relative to the interface, one can introduce, at least, two sets of the parameters; positional and orientational order parameters [5]. Textures of the LC films are produced by the average molecular orientation $\mathbf{n}=\langle\mathbf{u}_i\rangle$, called the director, and the fluctuation of the molecular orientation $\mathbf{u}_i$ with respect to $\mathbf{n}$ is expressed by the order parameters (OPs) $\overline{P_L}=\langle P_L[\cos(\mathbf{n}\cdot\mathbf{u}_i)]\rangle$, where $\langle\cdots\rangle$ denotes the statistical average, P_L are the Legendre polynomials of rank L. Monolayers at the air-water interface exhibit a number of features during compression of the films. For example, the OP $\overline{P_1}=\langle\cos(\mathbf{n}\cdot\mathbf{u}_i)\rangle$ plays a significant role in description of the 2D LC monolayers [6] because of the structural symmetry breaking at the interface, whereas that parameter is not so essential for describing the three-dimensional systems [7]. Since the LC molecules that form the Langmuir films posses strong polar group, the dipolar interactions among molecules can influence electro-optical properties of the 2D system. Recently, different techniques, Maxwell displacement current (MDC) [6] and optical second-harmonic generation (SHG) [8], have been usefully suggested to observe the dipole mechanism in the organic monolayers with C_∞ symmetry. The MDC and SHG signals allows us to determine the nonnormalized OPs $S_1(A)$ and $S_3(A)$, and the surface pressure π-A isothermal diagram, during compression of the cyanobiphenyl film. In particular, the MDC and SHG investigations of the 4-n-pentyl-4$'$-cyanobiphenyl (5CB) monolayers on the air-water interface during monolayer compression have been reported [9], and therefore a large data set is available for comparison with results from the theoretical routes. The theoretical treatment of the structural and thermodynamical properties of flexible amphiphilic molecules at the air-water interface is not an easy task [3]. This often requires a certain number of simplifying assumptions which may only be justified by comparison between the model predictions and experiments. But there is an additional avenue which would allow us to further examine the validity of our models; it is to carry out a theoretical treatment of the coupling between macroscopic film properties and molecular structure, and is then followed by comparisons of, for example, surface pressure π-A isotherm diagram with the experimental data. This implies that the set of the non-normalized OPs can be obtained from MDC and SHG measurements in monolayer film on the water as a function of the area A. Using these results for calculations, in the framework of the proposed model, the orientational dis-

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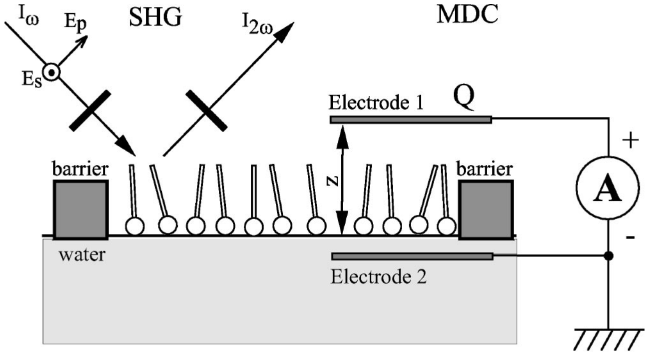


FIG. 1. Experimental setup for MDC and SHG measurements.

tribution function, average tilt angle, and entropy contribution to the Helmholtz free energy of the realistic mesogenic molecules, such as 5CB at the air-water interface, can be studied in the quasi two-dimensional system.

The outline of this article is as follows. A brief description of the MDC and SHG studies of molecular order and dielectric polarization of organic monolayers at the air-water interface is given in Sec. II. The molecular model of tilting Langmuir monolayer and numerical calculations for normalized $\overline{P_i}(A)$ $(i=1,\ 3)$, tilt angle $\overline{\theta}(A)$, π-A isotherm are given in Sec. III, for a monolayer film on the water surface. Conclusions are summarized in Sec. IV.

II. MAXWELL DISPLACEMENT CURRENT AND OPTICAL SECOND-HARMONIC GENERATION MEASUREMENTS

Figure 1 shows a schematic diagram of the MDC measurement coupled with the SHG one, where the electrode 1 is suspended in the air parallel to the water surface, and the electrode 2 is immersed in the water. In our experimental setup, the rectangular-shape *Langmuir* trough (60 mm $\times$150 mm in length and width, 10 mm in depth) composed of *polytetrafluoroethylene* is used, and it is filled with the pure water (electrical resistivity $>$17 MΩ cm). The electrode 1 is a transparent glass slide coated with indium-tin oxide, placed in the air parallel to the water surface at a distance of 1 mm. Electrode 2 is a gold wire (1 mm and 500 mm) and immersed in the water. These two electrodes 1 and 2 are connected to each other through an electrometer (Keithley 617). Assuming that the monolayers of 5CB on the water surface are prepared from a chloroform solution by the following compression of the film, the surface pressure diagram π-A, during the MDC measurements, can be determined by a *Wilhelmy* plate. The charge induced on the electrode 1, due to spontaneous polarization P_z, normal to the water surface, is given by formula [6,9]

$$Q=-\mu_z \ \ N \ \ S_1(A)/Z-C\phi_s, \tag{1}$$

and proportional to the OP $S_1(A)$. Here, N is the number of molecules under the electrode 1, μ_z is the projection of the molecular dipole moment on the normal to the water surface, C is the capacitance between the electrode 1 and the water surface, Z is the distance between the electrode 1 and the water surface, and ϕ_s is the water surface potential. The induced charge on the electrode 1 changes in accordance with the changing of both the orientational motion of molecules on the water surface and the surface density of molecules. Taking into account that the contributions due to changes of surface potential ϕ_s is negligibly small, it can safely be disregarded [6]. It is important to stress that the polar 5CB molecules, before compression, lies, due to the electrostatic *Coulomb* interactions between the cyanobiphenyl and water molecules, on the water surface. As a result, in the low density area A, i.e., in the region of immeasurably low surface pressure, the OP $S_1(A)$ to be equal to zero. Therefore, in the absence of the external field, the OP $S_1(A)=(Z/\mu_z N)Q$ of the monolayer can be determined over the entire range of molecular area A, by measuring the charge $Q=\int_0^t i(\tau)d\tau$, obtained from the MDC signal. Here the charge Q just corresponds to the difference in the induced charge on the electrode 1, at the molecular area $A=0$, at $\tau=0$, and $A=A_1$, at $\tau=t$.

On the other hand, the optical second-harmonic (SH) light is generated by laser irradiation, due to the quantum interaction between electrons in molecules and the external electric field [8]. If no account is taken of the local field correction factors such as *Lorentz factor*, the SH intensity in the direction $\mathbf{e}_{out}$ depends on the term $\mathbf{e}_{out}\cdot\mathbf{P}_N$, where $\mathbf{e}_{out}$ is a unit vector defined parallel to the SHG direction, and $\mathbf{P}_N$ is the nonlinear polarization of monolayers induced by laser irradiation. In the case of 5CB monolayers, where the second-order susceptibility is dominated by a single component along the molecular main axis, the SH intensity $I_{2\omega}$ generated from a monolayer with $C_{\infty v}$ symmetry is given by [10]

$$I_{2\omega}\propto[K_1S_1(A)+K_2S_3(A)]^2I_\omega^2. \tag{2}$$

Here, I_ω is the intensity of incident laser light, and K_1 and K_2 are functions of geometrical parameters of the optical arrangement, e.g., incident angle, output angle, polarizer angle, etc. Now, in the case of $K_1=0$ or $K_2=0$, one can formally determine the magnitude of the non-normalized OPs $S_1(A)$ and $S_3(A)$, respectively. It should be noted out that the similar expression given by Eq. (2) can be obtained, even when the local correction factors such as *Lorentz* factor is taken into consideration.

Briefly, the experimental setup consists of a Langmuir trough equipped with a two-electrode arrangement for the MDC measurement and the optical arrangement for the SHG measurement. It is a Q-switched Nd:YAG (yttrium aluminum garnet) laser (Big Sky Laser Technologies, Inc., maximum power 50 mJ, wavelength 0.532 μm, pulse duration $\leqslant$7 ns, fundamental pulse rate $\leqslant$15 Hz). Using this laser, monolayer is irradiated at an intensity of about 6 mJ with a pulse rate of 2 Hz. The laser spot size is about 56 mm^2. At the same time, both reflected and transmitted SH signals from floating monolayers can be detected using Eq. (2), and OPs $S_1(A)$ and $S_3(A)$ can be determined.

It should be pointed out that the present both MDC and SHG methods are unable to measure the second OP $S_2(A)$ of the flexible amphiphilic molecules at the air-water interface, and determination of the $S_2(A)$ still constitute a formidable

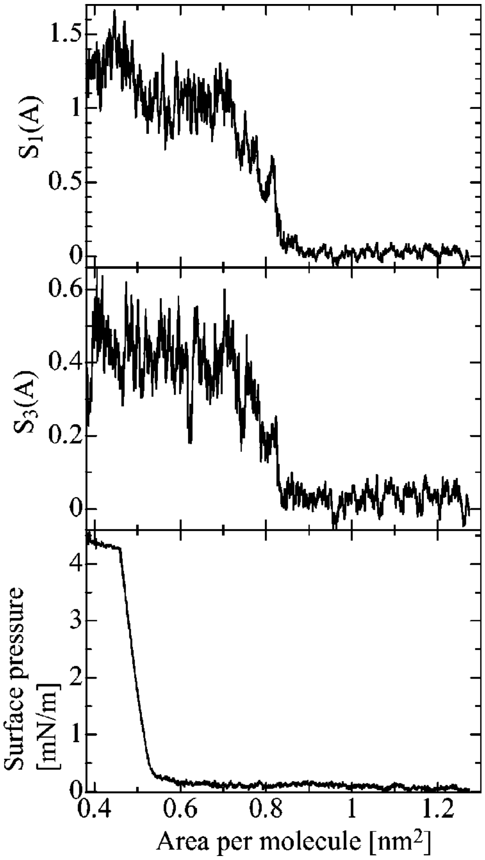
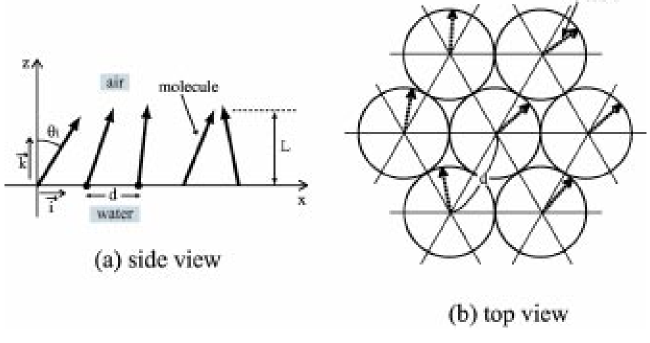


FIG. 2. Measured non-normalized OPs S_1 and S_3 and surface pressure $\pi(A)$ versus molecular area of a 5CB monolayer at the air-water interface.

task, where optical ellipsometric method [11] can be employed. In the following, we restricted ourselves only accounting for the first two OPs; $S_1(A)$ and $S_3(A)$, respectively. On the other hand, this limitation is counterbalanced by the specific property of monolayers arising from the symmetry breaking.

Figure 2 shows the non-normalized OPs $S_1(A)$ and $S_3(A)$, and the surface pressure-molecular area π-A isotherm of 5CB monolayers, determined by using both MDC and SHG techniques [9]. It should be noted that the OP $S_1(A)$, determined from MDC signals (not shown here), slightly different from the OP obtained using the SHG signals. The difference is not surprising because these measurements were done for different observation areas; MDC for 45 cm^2, whereas SHG for 56 mm^2, respectively. However main conclusion given in Secs. III and IV does not depend on this difference. In the following section, the OPs $S_1(A)$ and $S_3(A)$ determined by using the SHG technique, and the structural properties and the surface pressure π-A isothermal diagram is discussed in the framework of the molecular model, assuming that the randomly tilted polar 5CB molecules on the water surface are replaced by the collective tilted array of a unit vectors.



(a) side view

(b) top view

FIG. 3. Molecular model of monolayer composed of the tilted rodlike molecules: (a) view from the side, (b) view from the top.

III. STATISTICAL-MECHANICAL MODEL FOR DESCRIPTION OF THE TILTED MONOLAYER ON THE WATER SURFACE

Let us consider a model of tilted rodlike molecules with the heads group at the air-water interface, as shown in Fig. 3(a). Furthermore, each molecule is supposed to be surrounded by six neighbors in a hexagonal lattice [see Fig. 3(b)]. We restrict ourselves to a model of axially symmetric rods, applicable to the case of molecules freely rotating about their long axes and arbitrary tilted relative to the interface. The orientational order of the mesogenic molecules on the water surface is traditionally quantified in terms of OPs; however, the most complete description of the order is provided by the orientational distribution function. Having obtained the set of non-normalized OPs $S_1(A)$ and $S_3(A)$ of the flexible amphiphilic molecules at the air-water interface, derived from the MDC and SHG measurements (see also Fig. 2), one can calculate the normalized equilibrium orientational distribution function $f(\cos\theta_i)$ of the molecules on the water surface as

$$f(\cos\theta_i)=\frac{1}{4\pi}\sum_{L=0}^{\infty}\frac{2L+1}{2}\overline{P_L}P_L(\cos\theta_i), \tag{3}$$

where θ_i is the polar angle of the unit vector $\mathbf{u}_i$ along the molecular symmetry axis, and $P_L(\cos\theta_i)$ denote Legendre polynomials of any rank. The normalized OPs

$$\overline{P_i}=\frac{\int_{-1}^{+1}p_i(x)f(x)dx}{\int_{-1}^{+1}f(x)dx}, \tag{4}$$

where the function $f(x)$ as in Eq. (3), but with the non-normalized OPs, $i=1,3$, and

$$p_i(x)=\begin{cases} x, & i=1\\ \frac{1}{2}(5x^3-3x), & i=3, \end{cases}$$

are shown in Fig. 4(a), the average angle $\overline{\theta}=\int_0^{\pi}\theta_i f(\cos\theta_i)\sin\theta_i d\,\theta_i$, $d\overline{\theta}/dA$ as a function of the molecular area A, are shown in Figs. 4(b) and 4(c), respectively. The

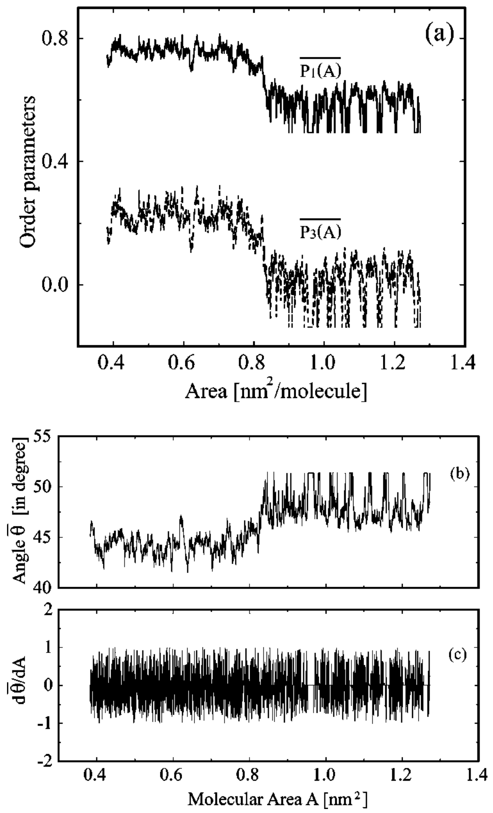


FIG. 4. (a) Normalized OPs $\overline{P}_1(A)$ (upper curve) and $\overline{P}_3(A)$ (lower curve) versus molecular area A of a 5CB monolayer at the air-water interface. (b) Plot of the average angle $\overline{\theta}(A)$ during compression of the film. (c) Same as (b), for $\partial\overline{\theta}(A)/\partial A$.

Helmholtz free energy of the system of N molecules occupying a volume V at the temperature T is given by the expression

$$F=\Phi_{tot}-TS, \tag{5}$$

where the entropy of the system can be written as

$$-S=-sN=k_BN\langle \ln f(\cos\theta_i)\rangle=k_BN\int_{-1}^{+1} f(x)\ln f(x)dx, \tag{6}$$

and Φ_{tot} is the total interaction energy of axially symmetric polar molecules at the air-water interface. When the Helmholtz free energy of the system is known, it is possible to calculate the surface pressure diagram $\pi=-[\partial F(A)/\partial A]$. Figure 5 shows the orientational entropy per 5CB molecule $s=S/N$ as function of the molecular area A. For calculation of the total interaction energy Φ_{tot} of the system composed of axially symmetric molecules, the hydrophilic heads of which are uniformly distributed on the water surface and the hydrophilic tails are directed away from the water surface, we use the molecular model of collective tilted rodlike polar molecules hinged by their ends to a water surface and separated by a certain distance each other. In the wide region of the molecular area, the MDC signals allows us to determine the dipole moment $\Delta_1(A)$ of the 5CB molecule at the air-water interface. We found from MDC measurement that with decreasing of the molecular area that dipole moment increases from zero, at the molecular area 0.6 nm$^2\leqslant A\leqslant 0.9$ nm^2, up to 0.5 D per molecule, at the molecular area 0.2 nm$^2\leqslant A\leqslant 0.6$ nm^2. Physically, this means that the initial dipole moment of the 5CB molecule ($\Delta\sim 5$ D) is the fully compensated, due to interactions with the water molecules, at the molecular area 0.6 nm$^2\leqslant A\leqslant 0.9$ nm^2, and that compensation is decrease up to 0.5 D per 5CB molecule, with decreasing of the molecular area. [9] That experimental observation allows us to consider the model of axially symmetric molecular rods, the hydrophilic heads of which are uniformly distributed on the water surface and the hydrophobic tails are directed away from the water surface and tilted at the average angle $\overline{\theta}(A)$ with respect to the unit vector **k** directed perpendicular to the interface.

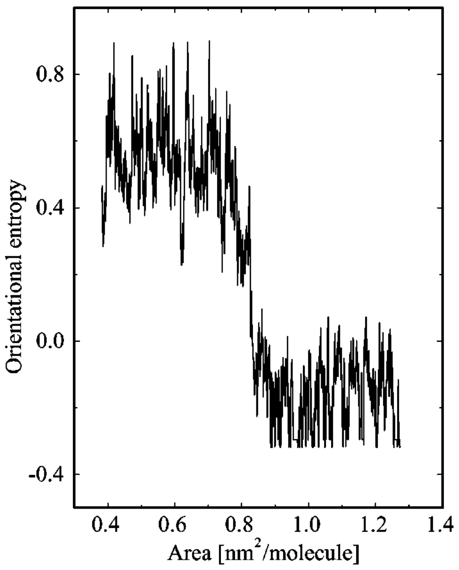


FIG. 5. The orientational entropy $s(A)$ dependence of the molecular area A of a 5CB monolayer at the air-water interface, calculated using Eq. (18), at $T=300$ K.

Consider the interaction energy of two tilted rodlike polar molecules of length L and diameter R, $R\ll L$, hinged by their ends to a water surface and separated by a distance $\overline{d}$ each other. The hinged ends will be referred to as the "heads" of the molecules and the free ends as "tails." The interaction between the rods consists of short-range repulsion, van der Waals attraction and dipole-dipole interactions with six neighbors in a hexagonal lattice and with one water molecule, modeled by hard core of radius d_1. The repulsive part of the potential is represented by a square-well steric repulsion Φ_{rp} taken to be infinitely large if the rods penetrate each other and zero otherwise. The tilted thin dielectric rods are described by two unit vectors, the vector $\mathbf{u}_i$ along the molecular symmetry axis and the vector $\mathbf{u}_{ij}$ connecting the molecular heads, as shown in Fig. 6. The distance between rods is equal $\overline{d}=d\sqrt{1-(\mathbf{u}_i\cdot\mathbf{u}_{ij})^2}$ and the overlapping length $l=L-2d|\mathbf{u}_i\cdot\mathbf{u}_{ij}|$, where d is the distance between two parallel rods. The van der Waals attraction per unit length of two tilted rods can be written as

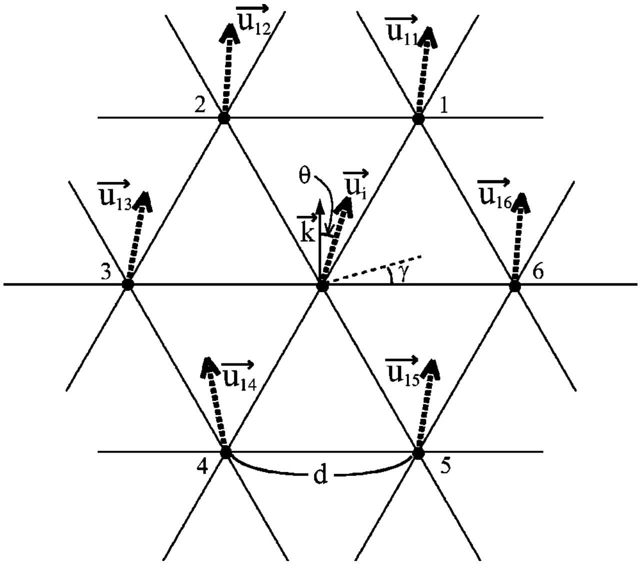


FIG. 6. Array of the rodlike molecules and molecular arrangement.

$$\Phi_{at}(ij)=-\frac{\epsilon_0 l}{\bar{d}^m}=-\frac{\epsilon_0 L}{d^m}\frac{1-\xi^{-1}|\mathbf{u}_i\cdot\mathbf{u}_{ij}|}{[1-(\mathbf{u}_i\cdot\mathbf{u_{ij}})^2]^{m/2}}, \tag{7}$$

where ϵ_0 is the energy parameter, $\xi=L/d$, and $m=5$. The dipolar interactions between LC molecules is defined by

$$\Phi_{dd}(ij)=\frac{\Delta_1^2}{\bar{d}^3}(\mathbf{u}_i\cdot\mathbf{u}_j-3\mathbf{u}_i\cdot\mathbf{u}_{ij}\mathbf{u}_j\cdot\mathbf{u}_{ij}), \tag{8}$$

where $\Delta_1\sim 0.5$ D is the magnitude of the molecular dipole moment corresponding to the tail of the 5CB molecule. The dipolar interaction between the hydrophilic head of the 5CB and the water molecules is defined as

$$\Phi_{dw}=\frac{\bar{\Delta}^2}{d_1^3}\cos\bar{\theta}, \tag{9}$$

where $\bar{\Delta}=\sqrt{\delta\Delta_2}$, $\delta\sim 1.4D$ is the dipole moment of the water molecule, $d_1\sim 0.096$ [nm] [12], and $\Delta_2=\Delta-\Delta_1$. Consider now the interaction of a rodlike molecules with its six neighbors in the hexagonal lattice and with one water molecule. The unit vectors $\mathbf{u}_i$ and $\mathbf{u}_{ij}$ take the form; $\mathbf{u}_i=\mathbf{u}_k=(\sin\bar{\theta}\cos\gamma_k,\sin\bar{\theta}\sin\gamma_k,\cos\bar{\theta})$ and $\mathbf{u}_{ij}=\mathbf{u}_{1k}=(\cos\bar{\gamma}_k,\sin\bar{\gamma}_k,0)$, respectively. Here $\gamma_k=\gamma+\pi k/3$, $\bar{\gamma}_k=\pi k/3$, $k=1,\ldots,6$, and the smallest azimuthal angle γ is chosen to be $-\pi/6\leqslant\gamma\leqslant\pi/6$ (see Fig. 6). Summation of the van der Waals attraction energy over the six neighbors gives us

$$\sum_{k=1}^{6}\Phi_{at}(1,k)=-\frac{\epsilon_0 L}{\bar{d}^m}\sum_{k=1}^{6}\frac{1-\xi^{-1}|\mathbf{u}_1\cdot\mathbf{u}_k|}{[1-(\mathbf{u}_1\cdot\mathbf{u_k})^2]^{m/2}}$$

$$=-\frac{\epsilon_{at}\xi}{A^{(m-1)/2}}[1-\xi\sin\bar{\theta}\mathcal{F}(\bar{\theta},\gamma)], \tag{10}$$

$$d=\sqrt{\frac{3}{2}A},\epsilon_{at}=6\left(\frac{2}{3}\right)^{(m-1)/2}\epsilon_0,$$

$$\mathcal{F}(\bar{\theta},\gamma)=\sin\bar{\theta}\left(\frac{2}{g_1(\bar{\theta},\gamma)}+\frac{1}{g_2(\bar{\theta},\gamma)}\right),$$

$$g_1(\bar{\theta},\gamma)=h_1(\bar{\theta},\gamma)^{m/2}=[4-\sin^2\bar{\theta}(\cos\gamma+\sqrt{3}\sin\gamma)^2]^{m/2},$$

$$g_2(\bar{\theta},\gamma)=h_2(\bar{\theta},\gamma)^{m/2}=(4-\sin^2\bar{\theta}\cos^2\gamma)^{m/2}.$$

Summation of the dipole-dipole energy over six neighbors LC molecules gives us

$$\sum_{k=1}^{6}\Phi_{dd}(1,k)=\frac{\Delta_1^2}{d^3}\sum_{k=1}^{6}(\mathbf{u}_1\cdot\mathbf{u}_k-3\mathbf{u}_1\cdot\mathbf{u}_{1k}\mathbf{u}_k\cdot\mathbf{u}_{1k})$$

$$=6\Delta_1^2\left(\frac{2}{3}\right)^{3/2}\frac{1}{A^{3/2}}. \tag{11}$$

The total interaction energy per 5CB molecule on the water surface is

$$\Phi_{tot}/N=\Phi_{rp}-\frac{\epsilon_{at}\xi}{A^{(m-1)/2}}[1-\xi\sin\bar{\theta}\mathcal{F}(\bar{\theta},\gamma)]+6(\Delta_1^2+\Delta_2^2)\times\left(\frac{2}{3}\right)^{3/2}\frac{1}{A^{3/2}}+\frac{\bar{\Delta}^2}{d_1^3}\cos\bar{\theta}. \tag{12}$$

It should be noted out that the water surface electric field E_0, originating from water surface charge density σ will penetrate the LC film and an additional contribution to the Helmholtz free energy should be accounted for by adding the term $-\int\mathbf{P}_s\cdot\mathbf{E}dA$, where $\mathbf{P}_s$ is the surface polarization. In the simplest case of the electric field $\mathbf{E}=E_0\mathbf{k}$, where $E_0=\sigma/\epsilon_0\bar{\epsilon}$ is the surface electric field of the charged water surface, ϵ_0 is the dielectric permittivity of free space, $\bar{\epsilon}=(\epsilon_\parallel+2\epsilon_\perp)/3$ is the average dielectric permittivity, $\epsilon_\parallel$ and $\epsilon_\perp$ are the dielectric constants parallel and perpendicular to the directioin $\mathbf{n}$, respectively. So, in our case, the surface polarization takes the form

$$\mathbf{P}_s=Nn_s\Delta(\sin\bar{\theta}\mathbf{i}+\cos\bar{\theta}\mathbf{k}), \tag{13}$$

where $n_s=1/A$ is the film surface charge density, $\mathbf{i}$ is a unit vector perpendicular to $\mathbf{k}$, and the surface polarization energy per unit area can be obtained by integrating the linear term $-\mathbf{P}_s\cdot\mathbf{E}$. The additional contribution to the Helmholtz free energy now can be written as

$$-\int\mathbf{P}_s\cdot\mathbf{E}dA=-\frac{\sigma\Delta}{\epsilon_0\bar{\epsilon}}\int\frac{\cos\bar{\theta}(A)}{A}dA, \tag{14}$$

and the final expression for the Helmholtz free energy per molecule is given by

$$F/N=\Phi_{rp}-\frac{\epsilon_{at}\xi}{A^{(m-1)/2}}[1-\xi\sin\overline{\theta}\mathcal{F}(\overline{\theta},\gamma)]+6(\Delta_1^2+\Delta_2^2)\times\left(\frac{2}{3}\right)^{3/2}\frac{1}{A^{3/2}}+\frac{\overline{\Delta}^2}{d_1^3}\cos\overline{\theta}+k_BT\int_{-1}^{+1}f(x)\ln f(x)dx+\frac{\sigma\Delta}{\epsilon_0\overline{\epsilon}}\int\frac{\cos\overline{\theta}(A)}{A}dA. \tag{15}$$

The general expression for the surface pressure $\pi=-\partial F(A)/\partial A$ can be written as

$$\pi=\pi_1+\pi_2+\pi_3, \tag{16}$$

where π_1, π_2, and π_3 are contributions to the surface pressure due to the total interaction energy $\pi_1=-(1/N)\times[\partial\Phi_{tot}(A)/\partial A]$, or

$$\pi_1=\epsilon_{at}\xi\frac{m-1}{2}\frac{1}{A^{(m+1)/2}}[\xi\sin\overline{\theta}\mathcal{F}(\overline{\theta},\gamma)-1]-\sqrt{24}\frac{\Delta_1^2+\Delta_2^2}{A^{5/2}}-\frac{\xi^2\epsilon_{at}}{A^{(m-1)/2}}[\cos\overline{\theta}\mathcal{F}(\overline{\theta},\gamma)+\sin\overline{\theta}H(\overline{\theta},\gamma)]\frac{\partial\overline{\theta}}{\partial A}+\overline{\Delta}_2^2\frac{\sin\overline{\theta}}{d_1^3}\frac{\partial\overline{\theta}(A)}{\partial A}, \tag{17}$$

due to the orientational entropy

$$\pi_2=T\frac{\partial s}{\partial A}, \tag{18}$$

and due to the surface polarization energy

$$\pi_3=\frac{\sigma\Delta_1}{\epsilon_0\overline{\epsilon}}\frac{\cos\overline{\theta}}{A}, \tag{19}$$

respectively. Here,

$$H(\overline{\theta},\gamma)=\cos\overline{\theta}\left(\frac{2}{g_1(\overline{\theta},\gamma)}+\frac{1}{g_2(\overline{\theta},\gamma)}\right)+\frac{m}{2}\sin\overline{\theta}\sin 2\overline{\theta}\left(\frac{2t(\gamma)}{h_1^{(m/2)+1}(\overline{\theta},\gamma)}+\frac{\cos^2\gamma}{h_2^{(m/2)+1}(\overline{\theta},\gamma)}\right),$$

and $t(\gamma)=(\cos\gamma+\sqrt{3}\sin\gamma)^2$. Both the first and second terms in the Eq. (17) gives a negative contributions to the total surface pressure π, due to the van der Waals and dipolar interactions, whereas the Eq. (18) gives a positive contribution to π, due to the orientational entropy (see also Fig. 5). The third and fourth terms in Eq. (17) are approximately equals [see Fig. 4(c)] to zero. It should be pointed out that both contributions π_1 and π_2 are $\sim$mN/m. In order to estimate the surface polarization contribution π_3 to the surface pressure π, one needs the data σ, Δ_1, $\overline{\theta}(A)$, $\epsilon_{\parallel}$, and $\epsilon_{\perp}$. In the following, we use the calculated data for the average angle $\overline{\theta}(A)$ [see Fig. 4(b)], and the dipole moment $\Delta_1(A)\leqslant 0.5$ D per 5CB molecule on the water surface, which has measured using the MDC technique. The values of $\overline{\epsilon}$ are determined using the temperature dependent coefficients $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ for 5CB obtained in Ref. [13]. So, for the monolayer film of 5CB molecules on the water surface with the charge density, for example, $\sigma=10^{-3}$ C/m^2 at $T=300$ K, one obtains $\pi_3\sim\mu$N/m, whereas $\pi_1+\pi_2\sim$mN/m, respectively. It should be pointed out that $\sigma=qn_w$, where $q=1.602\times10^{-19}$ C is the proton charge, and n_w is the water surface charge density. n_w can be estimated as $\sim1.6\times10^{16}$ m^{-2}, which agrees with experimental values $\sim10^{15}-10^{16}$ m^{-2} [12]. It is clear that the surface polarization contribution to the surface pressure can safely be disregarded at reasonable water surface charge density. In order to test the ability of the presented model, we carried out the calculation of the π-A diagram at $T=300$ K, for number of values of the energy parameter ϵ_{at}/Δ_1^2. The value of the azimuthal angle γ has chosen to be 0. Figure 7 shows the surface pressure $\pi=\pi_1+\pi_2$ dependence on the molecular area A, for ϵ_{at}/Δ_1^2 values: 1.0, 0.9, and 0.8, for curves 1, 2 and 3, respectively.

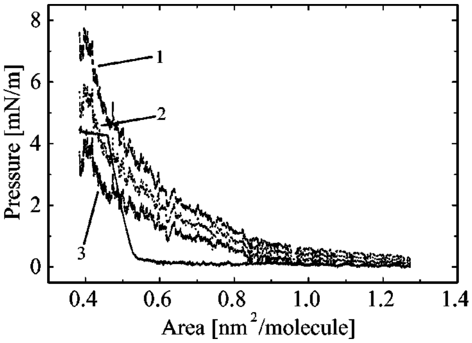


FIG. 7. π-A isotherm of the 5CB monolayer at the air-water interface, calculated using Eqs. (16)–(19), at three different values of the parameter ϵ_{at}/Δ_1^2 (from top to bottom): 1.0 (curve 1), 0.9 (curve 2), 0.8 (curve 3), respectively. The last curve (solid line) is obtained due to MDC technique.

It is important to stress that the inclusion of the orientational entropy mechanism, with a positive contribution to the surface pressure, lead to the reasonable agreement between calculated values and experimental results.

IV. CONCLUSION

In this paper, we investigate the orientational ordering and the surface pressure π-A isotherm in the liquid crystal monolayer of 4-n-pentyl-4′-cyanobiphenyl at the air-water interface. The set of non-normalized order parameters $S_i(A)$ ($i=1$, 3) , and the surface pressure π-A diagram are obtained both by the Maxwell displacement current and optical second harmonic generation methods. The equilibrium orientational distribution function $f(\cos\theta_i)$, the set of normalized OPs $\overline{P}_1(A)$ and $\overline{P}_3(A)$, and the orientational entropy $s(A)$ of that system are also investigated. We are aware, of course, the fact that the inclusion of the second OP is an important step toward the most general expression for the orientational distribution function. But at the present moment, the determination of the $\overline{P}_2(A)$ is still a formidable task. The surface pressure $\pi(A)$ is studied by combining the molecular model and the MDC technique. The molecular model implies that the randomly tilted two-dimensional array of the polar 5CB molecules at the air-water interface are replaced by the collective tilted, with the average polar angle $\overline{\theta}(A)$, rodlike polar molecules hinged by their ends to a water surface and separated by a certain distance from each other. That model is based on the van-der Waals and dipole-dipole interactions among LC neighbors and dipolar interaction between the hydrophilic head of the 5CB and water molecules. The van der Waals attraction is proportional to the contact area of two tilted polar molecules and gives the negative contribution to the surface pressure π, whereas the orientational entropy contribution to the π is positive. A balance between the dipolar, van der Waals and orientational entropy contributions is reflected in the growth of the surface pressure during monolayer compression. The relatively simple molecular model in combination with the experimental data obtained with high accuracy can provide a powerful tool for investigations both the structural and thermodynamics properties of real monolayer systems.

ACKNOWLEDGMENTS

One of us (A.V.Z.) gratefully acknowledges the financial support from of the research council of the K. U. Leuven, the Russian funds for Fundamental Research (Grant No. 01-03 32084) and Natural Research (Grant No. E00-5.0-154).

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