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Calculation of Molecular Orientational Order and Maxwell Displacement Current of Biaxial Molecules at the Air-liquid Interface

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On the basis of the electrodynamic interaction of biaxial molecules (with their larger permanent dipoles perpendicular to the molecular axes) with a liquid surface, we calculate the molecular orientational order and the Maxwell displacement current (MDC) of biaxial molecules with a thermostatical approach in the range of molecular area of immeasurably low surface pressure. It is shown that MDC generated by orientational change of the permanent dipoles along long molecular axes dominates the compression process shortly after the onset of the transition at A_0 from the planar surface alignment phase to the polar one, despite their smaller dipole moments than those perpendicular to the long molecular axes. This agrees with the fact that the MDC should change with the dipole moment along the long molecular axis. The results also reveal the thermodynamic motions of the dipoles parallel and perpendicular to the long molecular axis during the compression process.

KEYWORDS: biaxial, orientational order parameter, MDC, interface, organic monolayer films.

1. Introduction

The study of the electric properties of the monolayer at the air-liquid interface is a fascinating research topic because of its great potential applications.¹⁾ In the past few decades, it has undergone dramatic developments through experiments, and some theoretical methods in recent years have promoted a more profound understanding of various kinds of monolayers at the air-liquid interface. Among them, the thermostatical approach has been widely accepted as a useful method of probing molecular problems. The nematic order parameter which is represented as an average of the second Legendre polynomial has been developed for quite a few years, however it is not suitable for representing the polar orientational order of monolayers on a water surface.²⁾ In 1994, Sugimura *et al.* considered the amphiphile monolayer as half a membrane and thermostatically studied the orientational order of monopolar-molecule monolayers at the air-liquid interface without delving into the chemical details of the constituent molecules, using the order parameter represented by an average of first-order Legendre polynomials.³⁾ They then discussed the phase transition of 4-cyano-4'-5-alkyl-biphenyl (5CB) molecules from the planar surface alignment phase to the polar one in the range of low surface pressure during monolayer compression. Here the constituent polar molecules of monolayers were assumed to be rodlike and they had permanent dipoles in the direction parallel to the long molecular axis. As described in some electrodynamic textbooks,^{4,5)} the generation of interaction energy $W(\theta)$ acting between polar molecules and the water surface, which is the first step in statistical calculation, can be simplified by assuming an image dipole $\{(\epsilon_w - 1)/(\epsilon_w + 1)\}P$ at a symmetric position against the water surface. Here ϵ_w is the relative dielectric constant of water and P is the dipole moment of molecules. For half a membrane, $W(\theta)$ is calculated as³⁾

$$W(\theta) = -\frac{P^2}{16\pi\epsilon_0 l^3} \frac{\epsilon_w - 1}{\cos\theta \epsilon_w + 1}, \quad (1)$$

where l is the length of the molecule along its axis, θ is

the tilt angle of hydrocarbon chains away from the normal direction of the monolayer, and ϵ_0 is the permittivity of a vacuum. Despite the divergence of Maxwell displacement current (MDC) at the molecular area $A = A_0$ by monolayer compression, which is mainly caused by the take-off of very small molecules lying on the water surface, the model of half a membrane can reveal common features quite well for monopolar-molecule monolayer such as 5CB, with a permanent dipole along the long axis of rod molecule.³⁾ In this model, molecules are assumed to be rodlike with a length of l and A_0 is assumed to be πl^2 . However, the model of half a membrane cannot explain the present experimental results of MDC across monolayers consisting of biaxial molecules with a permanent dipole moment not parallel to the long molecular axis. For monolayers of cyclohexanecarboxylate-type liquid crystal (DON), with its larger permanent dipole perpendicular to the long molecular axis, the MDC generated by monolayer compression is rather small, around 10 fA (see Fig. 4(b)) after the phase transition from the planar surface alignment phase to the polar one, in comparison with 100 fA for 5CB, which was reported in our previous paper.⁶⁾ The polar orientational order S is a very important parameter in the investigation of any monolayer and it is the main contributor to MDC. S is defined as^{3,7)}

$$S = \langle P_1(\cos\theta) \rangle = \langle \cos\theta \rangle. \quad (2)$$

θ is the tilt angle of the long molecular axis away from the normal direction of the monolayer surface and P_1 is the first Legendre polynomial. S is proportional to the statistical mean dipole moment P_z in the direction normal to the monolayer surface. For monopolar molecules with a permanent dipole parallel to the long molecular axis, we may adopt either the Legendre polynomial definition or the physical definition given by eq. (2), in the same manner as discussed in our previous paper.³⁾ However for biaxial molecules, with a permanent dipole not parallel to the long molecular axis, we must adopt the following definition,

$$S = (P_{\parallel} \langle \cos\theta_{\parallel} \rangle + P_{\perp} \langle \cos\theta_{\perp} \rangle) / P$$

$$= (P_{\parallel} S_{\parallel} + P_{\perp} S_{\perp}) / P, \quad (3)$$

where P_{\parallel} and P_{\perp} are the permanent dipoles along the long molecular axis and perpendicular to the molecular axis, respectively, θ_{\parallel} and θ_{\perp} are their corresponding tilt angles away from the normal direction of the monolayer (see Fig. 1), $\langle \rangle$ denotes a thermodynamic average, and P is the total dipole momentum of the molecule, which is expressed as $\sqrt{P_{\parallel}^2 + P_{\perp}^2}$. From the expression above, it is obvious that S is the degree of contribution by molecule dipoles to the normal direction with respect to the water surface on the basis of the statistical average. In this paper, we use this definition with a membrane model to discuss the contribution of polarization to the MDC of biaxial molecules such as DON on a water surface in the range of low surface pressure after the phase transition from the planar surface alignment phase to the polar one. We then use this model to explain the experimental results for DON103, which differ from those for 5CB in the magnitude of the generation of MDC.

2. Calculation

As a model, we consider a biaxial monolayer film with a permanent dipole not parallel to the molecular axis (e.g. DON) on an air-water surface, as shown in the inset of Fig. 1, which illustrates the interaction of biaxial molecules with the water surface. R and R' are carbon chains and DON103 is a mixed molecule of three types of DON with R/R' of C₃/C₂ (23%), C₄/C₅ (38%) and C₅/C₁ (39%). Although the direction of the C=O covalent

bond is not perpendicular to the long molecular axis in the actual DON molecule, we assume, in the present analysis, that the biaxial molecule is simplified to a rodlike axis with a length l , with the smaller point dipole P_{\parallel} along the long molecular axis at the midpoint, and the larger dipole P_{\perp} at a distance l_0 perpendicular to the long molecular axis because of the C=O covalent bond direction. This model is different from the conventional treatment which was discussed by Sugimura *et al.*,³⁾ because it has a dipole moment P_{\perp} perpendicular to the long molecular axis. The system experiences a three-degree-of-freedom thermodynamic motion, i.e., the motion of the rodlike long axis in the azimuthal plane, and the revolution and rotation of the long molecular axis shortly after the onset of the transition at the molecule area $A/A_0 = 1$ by monolayer compression. The revolution gives no thermostatical contribution to MDC because the orientational order parameter S defined as eq. (3) may not change, i.e., the vertical component of the dipole moment of molecules does not change. In contrast, the change in the distance of P_{\perp} from the liquid surface while rotating, should lead to MDC generation. The rotation angular displacement φ and tilt angle θ_{\parallel} , θ_{\perp} at an arbitrary position, as shown in Fig. 1(b), satisfy

$$\cos \theta_{\perp} = \cos \varphi \sin \theta \quad (4)$$

and

$$\theta_{\parallel} = \theta. \quad (5)$$

The critical molecular area A_0 is again estimated to be πl^2 . The molecules are assumed to lie on the water surface at $A > A_0$ and align in the range of $0 \leq \theta \leq \theta_A$ due to the effect of hard core intermolecular forces in the range of molecular area $A < A_0$, where $\theta_A = \arcsin(\sqrt{A/A_0})$. Therefore, in the range $A > A_0$, the order parameter S defined by eq. (3) is zero (see Fig. 1) and MDC I is not generated by monolayer compression, as expected from eq. (23). In the following, we confine our discussion to monolayers in the range $A < A_0$. At first, we neglect the interaction between P_{\perp} and P_{\parallel} because of its independence in a molecule. Furthermore, the interaction among molecules can be neglected in the region $0.6 < A/A_0 < 1$, because the interaction energy among molecules $W_d = 11.0342P^2/4\pi\epsilon_0 a^3$ (P the permanent dipole moment, a the distance between the most neighboring two molecules)⁸⁾ is smaller than the interaction energy between water and molecule W_s given by eq. (6) in this range, under the assumption that $a = 4\sigma l \sin \theta_A$ ($0 < \sigma < 1$). Here σl is the distance from the water surface. In the following, for simplicity, we discuss the generation of MDC considering only the interaction between molecules and the water surface, because the main interaction in our work is the generation of MDC shortly after the onset of transition at the molecular area $A/A_0 = 1$. By introducing an image dipole $\{(\epsilon_w - 1)/(\epsilon_w + 1)\}P$ at a mirror position with respect to the water surface (see Fig. 1), the effect of interface interaction working between a dipole with a permanent dipole moment P and the water surface is obtained as

$$W(\theta) = -\frac{P^2(\cos^2 \theta + 1)}{64\pi\epsilon_0 d^3} \frac{\epsilon_w - 1}{\epsilon_w + 1}. \quad (6)$$

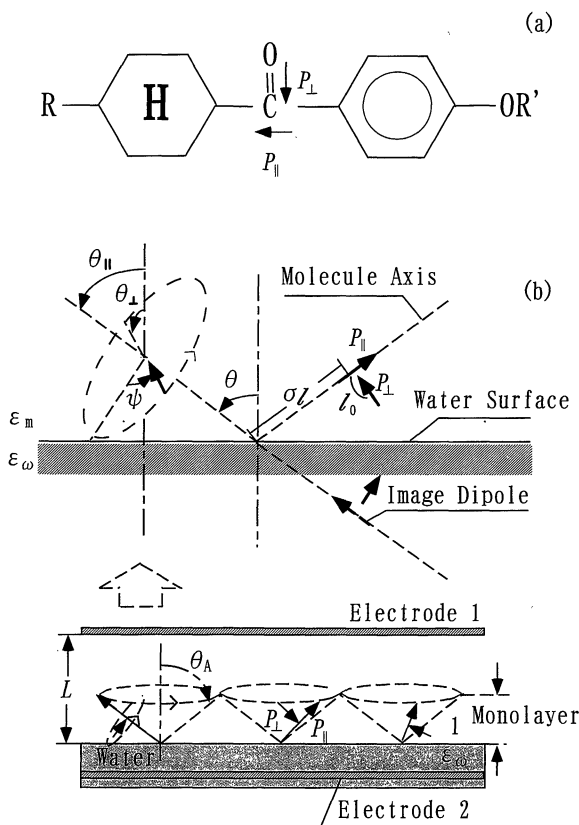


Fig. 1. (a) Molecular structure of DON and (b) sketch of the model for the biaxial-molecule monolayer at an air-liquid interface.

Here d is the distance between the dipole and the water surface. For P_{\perp} , d satisfies

$$d = \sigma l \cos \theta - l_0 \cos \varphi \sin \theta, \quad (7)$$

where σl is the distance between the point dipole P_{\parallel} and the water surface along the long molecular axis. Under the approximation of

$$d^{-3} \approx (\sigma l \cos \theta)^{-3} \left(1 + 3 \frac{l_0}{\sigma l} \tan \theta \cos \varphi \right) \quad (8)$$

and using eqs. (4) and (6), the interaction energy $W(\theta_{\perp})$ of P_{\perp} can be written as

$$W_{\perp}(\theta) = -\chi_{\perp} kT \frac{\sin^2 \theta \cos^2 \varphi + 1}{\cos^3 \theta} \times \left(1 + 3 \frac{l_0}{\sigma l} \tan \theta \cos \varphi \right) \quad (9)$$

with

$$\chi_{\perp} = \frac{P_{\perp}^2}{8\pi\epsilon_0 l^3 kT} \frac{\epsilon_w - 1}{\epsilon_w + 1}. \quad (10)$$

We must estimate the limit of the approximation eq. (8), because $l_0 \tan \theta / (\sigma l) = \infty$ in the case of $\theta = \pi/2$. Taking DON as a typical example, we substitute $P_{\perp} = 2.5$ D, $\sigma l = 1.0$ nm,⁹⁾ and $l_0 = P_{\perp} / (2e) = 0.025$ nm, and obtain $\chi_{\perp} = 9.2 \times 10^{-3}$ and $\theta < 76^\circ$ if $l_0 \tan \theta / (\sigma l) < 0.1$. That is, the calculation based on eq. (8) is reasonable within the region $[0^\circ, 76^\circ]$ with a deviation under 10%. On the other hand, to obtain the interaction energy of P_{\parallel} , substitute

$$d = \sigma l \cos \theta_{\parallel} \quad (11)$$

and eq. (5) into eq. (6) such that $W(\theta)$ becomes

$$W_{\parallel}(\theta) = -\chi_{\parallel} kT \frac{\cos^2 \theta + 1}{\cos^3 \theta}, \quad (12)$$

where

$$\chi_{\parallel} = \frac{P_{\parallel}^2}{8\pi\epsilon_0 l^3 kT} \frac{\epsilon_w - 1}{\epsilon_w + 1}. \quad (13)$$

For DON, a typical value of $P_{\parallel} = 0.8$ D leads to $\chi_{\parallel} = 1.0 \times 10^{-3}$. The monolayer is treated as a boson system which satisfies the Boltzmann distribution

$$f(\theta, \varphi) = \frac{e^{-W/kT}}{Z}, \quad (14)$$

where $W = W_{\perp} + W_{\parallel}$. As in the region $[0^\circ, 76^\circ]$, $W_{\perp}/kT \ll 1$ and $W_{\parallel}/kT \ll 1$, the single-particle partition is

$$Z = \int_0^{\theta_A} \int_0^{2\pi} e^{-(W_{\perp} + W_{\parallel})/kT} d\varphi \sin \theta d\theta = 2\pi[(1 - \cos \theta_A) + Z_{\perp} + Z_{\parallel}], \quad (15)$$

where

$$Z_{\perp} = \int_0^{\theta_A} \left(-\frac{W_{\perp}}{kT} \right) \sin \theta d\theta = \left(\frac{\ln \cos \theta_A}{2} - \frac{3 \cos^2 \theta_A - 1}{4 \cos^2 \theta_A} \right) \chi_{\perp} \quad (16)$$

and

$$Z_{\parallel} = \int_0^{\theta_A} \left(-\frac{W_{\parallel}}{kT} \right) \sin \theta d\theta$$

$$= \left(-\ln \cos(\theta_A) + \frac{1 - \cos^2 \theta_A}{2 \cos^2 \theta_A} \right) \chi_{\parallel}. \quad (17)$$

Z_{\perp} and Z_{\parallel} are the rectifications to the free space, which is expressed by $2\pi(1 - \cos \theta_A)$. With the Boltzmann distribution defined as eq. (14), the orientational order of P_{\perp} is given by

$$S_{\perp} = \int_0^{\theta_A} \int_0^{2\pi} \sin \theta \cos \varphi \frac{e^{-(W_{\perp} + W_{\parallel})/kT}}{Z} d\varphi \sin \theta d\theta. \quad (18)$$

A simple calculation of eq. (18) under the approximation $e^{-(W_{\parallel} + W_{\perp})/kT} \approx 1 - (W_{\parallel} + W_{\perp})/kT$ leads to

$$S_{\perp}(\theta_A) = \frac{1}{Z} \frac{3\pi\chi_{\perp} l_0}{4l} \left(\frac{32}{3} + \frac{7}{3 \cos^3 \theta_A} - \frac{10}{\cos \theta_A} - 3 \cos \theta_A \right). \quad (19)$$

Z is also a function of θ_A expressed by eq. (15). As we can see from eq. (19), the order parameter of P_{\perp} is small because of a small χ_{\perp} . The numerical $S_{\perp} - A/A_0$ relation of DON is presented in Fig. 2(a). It should be noted here that S_{\perp} is plotted as the solid line in the range $A/A_0 < 0.94147$ because of the calculation limitation of $0^\circ < \theta_A < 76^\circ$. The orientational order of the dipole P_{\perp} perpendicular to the long molecular axis is very small, around a scale of 0.01, and quickly reduces to zero shortly after the onset of the transition. It is obvious that when $A/A_0 \rightarrow 0$, i.e., $\theta \rightarrow 0$, $S_{\perp} \rightarrow 0$, which corresponds to the state that P_{\perp} is parallel to the water surface. This result can also be easily obtained from eq. (19). On the other hand, in the case of P_{\parallel} , the order parameter S_{\parallel} should be

$$S_{\parallel} = \frac{\int_0^{\theta_A} \int_0^{2\pi} e^{-(W_{\parallel} + W_{\perp})/kT} \cos \theta \sin \theta d\varphi d\theta}{Z}. \quad (20)$$

A similar calculation of eq. (20) yields

$$S_{\parallel} = \frac{(1 - \cos^2 \theta_A) + \left(\cos \theta_A - \frac{1}{\cos \theta_A} \right) (2\chi_{\parallel} + \chi_{\perp})}{2[(1 - \cos \theta_A) + Z_{\perp} + Z_{\parallel}]}, \quad (21)$$

which is also depicted in Fig. 2(b). The orientational order of the dipole P_{\parallel} along the molecular axis presents a similar shape as obtained by Sugimura *et al.* with the half-membrane treatment.³⁾ The total orientational order S defined by eq. (3) is presented in Fig. 2(c). The total MDC I generated by monolayer compression with the constant speed $\gamma = -dA/dt$ is given by

$$I = I_{\perp} + I_{\parallel} = \frac{B\gamma}{L} \left(\frac{P_{\perp} S_{\perp} + P_{\parallel} S_{\parallel}}{A^2} - \frac{d(P_{\perp} S_{\perp} + P_{\parallel} S_{\parallel})}{A dA} \right). \quad (22)$$

Here B is the working area of the electrode, and L is the distance between the water surface and the electrode suspended in air above the water surface in the measurement of MDC (electrode 1 in Fig. 4(a)). In the derivation of eq. (22), we assumed that the effect of the surface potential change of water is negligible, because the change is gentle in comparison with the effect of the change in the order parameter S by monolayer compression, as described in our previous report.⁷⁾ With the S definition

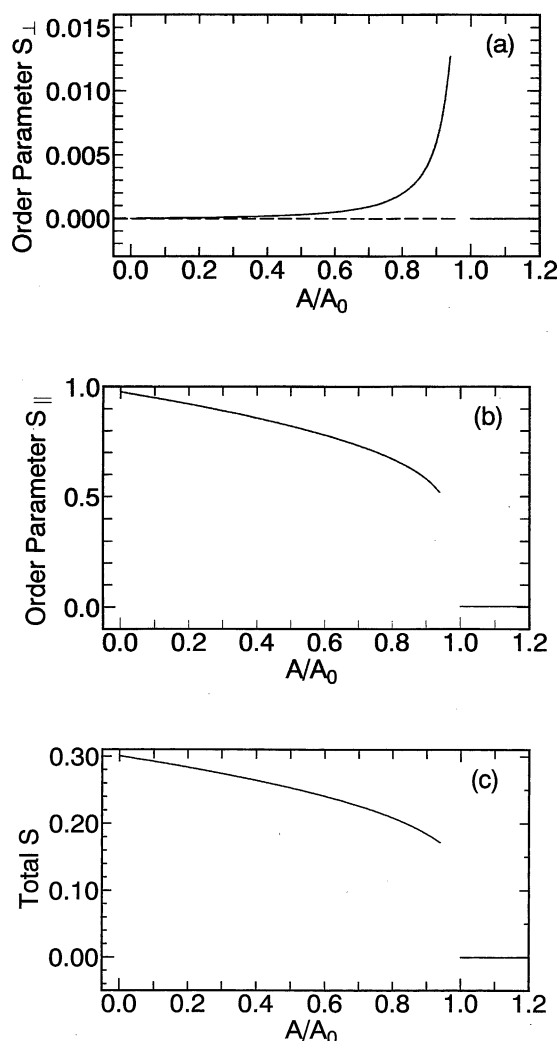


Fig. 2. (a) Order parameter S_{\perp} undergoes a sharp decrease to zero as the monolayer is compressed, which reveals that S_{\parallel} is the main contributor to MDC shortly after the onset of transition. (b) Relative area dependence of order parameter S_{\parallel} . (c) Total parameter S exhibits the same shape as S_{\parallel} .

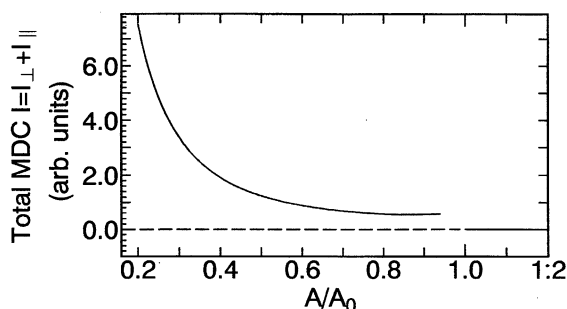


Fig. 3. The theoretical total MDC I .

for biaxial molecules of eq. (3), eq. (22) can be rewritten in the standard form

$$I = \frac{BP\gamma}{L} \left(\frac{S}{A^2} - \frac{dS}{AdA} \right). \quad (23)$$

Due to the extremely complicated expression for I , we do not give its explicit form but show only a graph (Fig. 3).

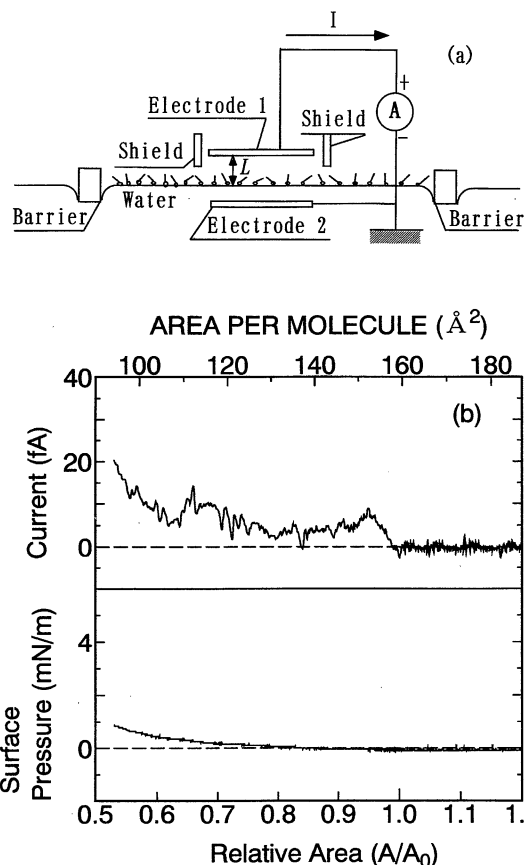


Fig. 4. (a) Schematic diagram of the experimental setup used for the study of DON103 and (b) displacement current of DON103 monolayer with a constant compression speed γ of 40 mm/min.

3. Experiment

Figure 4(a) demonstrates the experimental setup in the study of DON103, which was the same as that used in our previous study.⁷⁾ Briefly, the trough has a rectangular shape with an area of 1,050 cm². At the center of the trough, electrode 1 with a working area of 44.2 cm² is placed parallel to and at a distance of 1.0 ± 0.05 mm above the water surface. The two electrodes are short-circuited with a picoampere electrometer measuring the MDC generated as the monolayer is compressed or expanded. Monolayers of DON103 are spread from a chloroform solution onto the water surface using a microsyringe. The monolayers on the water surface are compressed from both sides of the trough with the aid of two barriers moving simultaneously in opposite directions at room temperature. As shown in Fig. 4(b), in the region $A/A_0 > 1$, before the onset of the transition at the molecular area $A/A_0 = 1$, MDC I is zero. In contrast, after the onset of the transition, MDC I is about several fA in the range $0.5 < A/A_0 < 1.0$. The data obtained by MDC measurement was reproducible within the constraint of our experiment.¹⁰⁾

4. Discussion and Conclusion

We have calculated the orientational order of the molecules with a permanent dipole moment not parallel to the long molecular axis and MDC in the region $[0^\circ, 76^\circ]$, i.e., in the region $0 < A/A_0 < 0.94147$, and

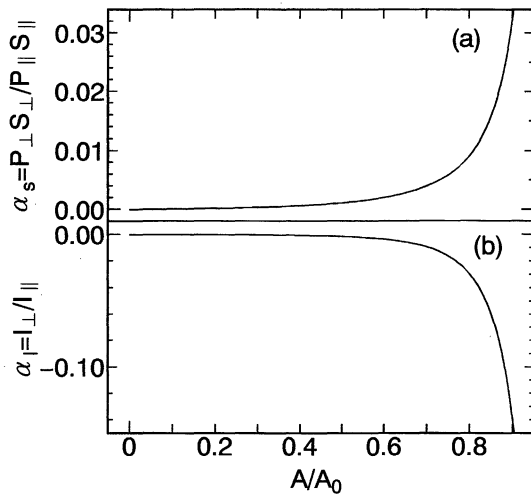


Fig. 5. The comparison between the two dipoles P_{\perp} and P_{\parallel} . (a) α_S shows that the effect of P_{\perp} is negligible shortly after the onset of the transition. (b) Ratio α_I shows the opposite MDC direction and a great discrepancy between the contributions of P_{\perp} and P_{\parallel} .

several graphs and experimental MDC are shown. For better comparison between P_{\perp} and P_{\parallel} in the contribution of MDC, we designate two ratios:

$$\alpha_S = \frac{P_{\perp} S_{\perp}}{P_{\parallel} S_{\parallel}} \quad (24)$$

and

$$\alpha_I = \frac{I_{\perp}}{I_{\parallel}}, \quad (25)$$

which are shown in Fig. 5. Figure 5(b) also reveals that the direction of MDC created by P_{\perp} is different from that by P_{\parallel} , and that the total orientational order S and MDC of biaxial molecules are mainly created due to the dipole moment P_{\parallel} parallel to the long molecular axis despite its much smaller dipole moment in comparison with the dipole moment P_{\perp} perpendicular to the long molecular axis, as the monolayer is compressed. This conclusion is also supported by the finding that the total orientational order S (Fig. 2(c)) defined by eq. (3) has the same appearance as S_{\parallel} (Fig. 2(b)). These results coincide with the fact that molecules with different main chain lengths should exhibit the onset of the MDC generation at the molecular area $A_0 = \pi l^2$, in a manner similar to the generation of nCBs.⁶⁾ Obviously, liquid crystal monolayers on a water surface exhibit various phases during monolayer compression, and the interaction among molecules becomes increasingly important as monolayers are further compressed.⁸⁾ However, in our present model, we only take into account the electrostatic interaction between molecules and the water surface. Thus it should be noted here that the present model is useful only in the range of low surface pressure, just after the phase transition at the molecular area A_0 from the planar alignment phase to the polar one, because the dipole moment parallel to the long molecular axis is the dominant con-

tributor to displacement current. It is also obvious that the MDC of 5CB generated due to a much larger permanent dipole along the long molecular axis should be much larger than that of DON. The MDC generation of DON103 shown in Fig. 4(b) is very small and it flows in the positive direction. The shape of the MDC is similar to that shown in Fig. 3 obtained by calculation. Taking DON103 as an example, the magnitude of MDC in the range of $0.5 < A/A_0 < 0.94147$ is several fA by simple calculation, which is within the same scale as the experimental results (Fig. 4). Here it should be noted that the calculation above is restricted to within $[0^\circ, 76^\circ]$. At the beginning of the standing-up of DON103 molecules, i.e., in the region $0.94147 < A/A_0 < 1$, the deviation of calculated values obtained in this work becomes bigger. On the other hand, as $A/A_0 \rightarrow 1$, the O atom in the C=O bond still rests on the monolayer because the C=O bond is more hydrophilic than the C-C bond. Thus at this stage the monolayer is half a membrane and MDC is mainly created by P_{\perp} in a manner similar to that described by Sugimura *et al.*'s calculation.³⁾ The reason why there was not such a large peak at the onset of transition as that predicted by the half-membrane model is that at $\theta = \pi/2$, the size of the molecule should be considered and the interaction energy (eq. (1)) should be rectified into some other form in which the convergence at A/A_0 is avoided. As we discussed in the present paper, molecules are assumed to lie and stand up on a water surface and not to be pulled into the water. For further detailed discussion, we must take this effect into consideration. However this is a future task.

It is now possible to explain the compression process. Immediately after the onset of the transition at the molecular area $A/A_0 = 1$, P_{\perp} is the main contributor to MDC, but its contribution decreases exponentially as the molecule area is further compressed. In a very short time, P_{\parallel} replaces P_{\perp} and dominates the contribution to MDC in the compression process thereafter.

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