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Analysis of dielectric relaxation phenomena with molecular orientational ordering in monolayers at the liquid-air interface

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Starting from the Debye theory of rotational Brownian motion, we analyzed the dielectric relaxation phenomena with molecular orientational ordering in Langmüir film on a water surface, assuming that the orientational distribution of the constituent rodlike polar molecules is ruled by Boltzmann statistics. The transient behavior of the polar molecules induced by the application of step compression at the molecular area $A = A_i (< A_c)$ is discussed with taking account of the friction constant of monolayer ξ, and the dielectric relaxation time τ. Here A_c is the critical molecular area defined as πl^2 (l: the length of rodlike polar molecule). The orientational order parameter S of monolayers and Maxwell displacement current (MDC) at the dielectric relaxation process were obtained, for the first time, with the consideration of ξ and τ. On the basis of the analysis developed here, we examined the generation of MDC across 4-cyano-4′-5-alkyl-biphenyl (5CB) Langmüir film by monolayer compression.

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I. INTRODUCTION

Over the past several decades, the dielectric relaxation phenomena in dielectric materials including organic materials, lipids, and liquids have been a subject of many studies in various fields: physics, chemistry, electronics, biology, etc. One of the most important contributions in these fields was the idea developed by Debye in 1913. He studied the rotational Brownian motion of molecules with permanent electric dipoles in liquids, and developed a method for the analysis of the dielectric relaxation phenomena [1]. On the basis of Debye philosophy, many studies of the dielectric relaxation phenomena such as polarization and depolarization in dielectric bulk materials have been carried out for the past ten years [2–4]. Recently these studies have been applied to the investigation of the dielectric property of ultrathin films such as organic mono- and multilayer films [5]. Tanguy and Hesto studied the polarization effects associated with the initial heating of orthphenanthrolin multilayers sandwiched between metal electrodes [6]. The investigation by Jonscher on the thermally stimulated depolarization current (TSD) flowing across organic multilayers on the basis of the so-called ''Universal law'' leads to a different theoretical approach to TSD [7]. Unfortunately, following the Debye model, few theoretical expressions were successfully constructed for analyzing the dielectric relaxation phenomena in monolayers on a material surface. Further, it was very difficult to obtain the reproducibility in the TSD measurement, in particular, in the measurement of one-layer films sandwiched between top and base electrodes, principally due to the destruction of film by the application of the top electrode. In our previous papers [8,9], we developed an electrical technique, that allows orientational change in polar molecules on a water surface to be probed by measuring the Maxwell displacement current (MDC). The MDC is the transient current generated across an electrode suspended in air and a material surface, e.g., due to the orientational charge in polar molecules on the material surface. The MDC measurement can give essential information on the polar orientational order in monolayers at the liquid-air interface even in the range of immeasurably low surface pressure. Here the orientational order is defined as $S = \langle \cos\theta \rangle$, θ is the tilt angle of rodlike polar molecules away from the normal direction of the monolayer, and $\langle\ \rangle$ denotes a thermodynamics average. Thus the technique is suitable for studying the dielectric relaxation phenomena accompanying the orientational ordering and disordering of monolayers on a material surface, where the relaxation phenomena are induced by external stimulation, such as monolayer compression and photoirradiation. Further, in our previous paper [8], we applied a classical mean field approach to the calculation of the generation of Maxwell displacement current due to the ordering and disordering of organic multilayers, under the assumption that the orientational change in the constituent molecules is quick enough to respond to the external stimulation, such as surface pressure application and thermal stimulation. This approach is unfortunately restricted within the frame of equilibrium thermodynamical statistics and it is necessary to combine the Debye method with the monolayer model discussed in our previous papers [10,11] for a better understanding of the dielectric relaxation phenomena in monolayers. For example, nonequilibrium phenomena which happen at the onset of phase transition will be clarified. In this paper, we discuss the dielectric relaxation time of monolayers on a water surface on the basis of the Debye rotational Brownian motion equation [12]. We then rectify the orientational order parameter of monolayers during the dielectric relaxation of monolayers, with consideration of relaxation time τ and the monolayer viscosity ξ. Finally, we examine the generation of Maxwell displacement current across 4-cyano-4′-5-alkyl-biphenyl(5CB) Langmüir film in the range of immeasurably low surface pressure at the molecular area close to the onset phase transition from the planar surface alignment phase to the polar orientational one by monolayer compression.

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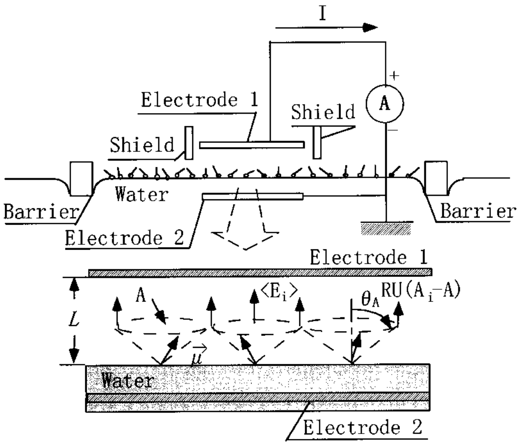

FIG. 1. Sketch of Debye Brownian motion model of Langmüir film at an air-liquid interface.

II. ANALYSIS

Figure 1 shows a model of a monolayer on a water surface, which is used for the following analysis. The monolayer consists of rodlike polar molecules with a length l. Each molecule has a permanent dipole moment μ in the direction along its long axis, and it stands on a water surface at a tilt angle θ away from the normal direction to the water surface. The orientational distribution of the constituent molecules is ruled by Boltzmann statistics. It is convenient here to start from the rotational Debye-Brownian equation [12]

$$\frac{\partial \omega(\theta,t)}{\partial t}=\frac{1}{\xi \sin\theta}\frac{\partial}{\partial \theta}\left[\sin\theta\left(kT\frac{\partial \omega}{\partial \theta}+V\sin\theta\omega(\theta,t)\right)\right], \tag{1}$$

where $\omega(\theta,t)$ is the possibility function representing the possibility of the molecules standing on a water surface at a tilt angle θ at time t. ξ is the friction constant of monolayer and V the interaction form function excluding the angular portion. V contains dipole-surface interaction, dipole-dipole interaction, and equivalent additional piezoelectrical interaction produced by monolayer compression. In the present analysis, only dipole-dipole interaction and equivalent additional piezoelectrical interaction energy are taken into consideration in the mean field approximation, because the dipole-surface interaction is negligibly small in comparison with the other two interactions in the region of the molecular area $A<A_c$ [13]. Here A_c is the critical molecular area $(=\pi l^2)$ at which molecules lying on a water surface due to the dipole-water surface interaction stand up by monolayer compression. The first term on the right hand side of Eq. (1) represents the possibility flow due to the thermal motion of the environment obeying the law of Fick. The second term is the flow due to the effect of internal interaction working among molecules and external interactions produced by monolayer compression. Equation (1) is just a continuity equation of possibility flux flow and it is rewritten as

$$\frac{\partial \omega}{\partial t}+\boldsymbol{\nabla}\cdot\mathbf{j}=0. \tag{2}$$

Here j is the possibility flux flow given by

$$\mathbf{j}(\theta_A,t)=-\left[\frac{kT}{\xi}\frac{\partial \omega}{\partial \theta}+\frac{V}{\xi}\sin\theta\omega\right]\mathbf{e}_\theta. \tag{3}$$

It is understandable that only the portion along direction $\mathbf{e}_\theta$ exists because of the rotational motion of molecules on a material surface, as shown in Fig. 1. As described in our previous papers [10,11], under a mean field approximation, it is reasonable to assume that the motion of rodlike polar molecules is restricted within $0<\theta<\theta_A$, where $\theta_A=\sin^{-1}\sqrt{A/A_c}$, principally due to effects of hard core intermolecular forces. Thus at $\theta=\theta_A$, the following boundary condition concerning the possibility flux flow is satisfied:

$$\mathbf{j}|_{\theta=\theta_A}=\mathbf{0}. \tag{4}$$

At the equilibrium state, there is no possibility flux flow among molecules. Thus the possibility flux $j(\theta,t)$ should be

$$\mathbf{j}(\theta,t)=-\left[\frac{kT}{\xi}\frac{\partial \omega}{\partial \theta}+\frac{V}{\xi}\sin\theta\omega\right]_{\mathrm{eq}}\mathbf{e}_\theta=0, \tag{5}$$

that is,

$$\frac{kT}{\xi}\frac{d\omega}{d\theta}=-\frac{V}{\xi}\sin\theta\omega. \tag{6}$$

From Eq. (6), we obtain

$$\omega(\theta)\sim\exp\left\{-\frac{V}{kT}\cos\theta\right\}. \tag{7}$$

In our previous studies, we used Eq. (7) for the calculation of the dielectric constant of monolayers [13], TSD current across monolayers [11], and MDC current I_{eq} generated by monolayer compression [8].

III. CALCULATION

With the orientational order parameter of monolayers on a water surface, which is defined as [10]

$$S=\int_0^{\theta_A}\cos\theta\omega(\theta,t)\sin\theta d\theta,$$

Eq. (1) can be used to find the order parameter S during monolayer compression. S satisfies the following equation:

$$\frac{\partial S}{\partial t}=\int_0^{\theta_A}\cos\theta\frac{1}{\xi \sin\theta}\frac{\partial}{\partial \theta}\left[\sin\theta\left(kT\frac{\partial \omega}{\partial \theta}+V\sin\theta\omega(\theta,t)\right)\right]\sin\theta d\theta. \tag{8}$$

Integrating in parts and considering the boundary condition given by Eq. (4), we get

$$\frac{\partial S}{\partial t}=\int_0^{\theta_A}\frac{1}{\xi}\sin^2\theta\left(kT\frac{\partial \omega}{\partial \theta}+V\sin\theta\omega\right)d\theta. \tag{9}$$

In order to examine the dielectric relaxation phenomena by monolayer compression, we assume here that a step additional interaction $RU(A_i-A)$ is produced in monolayers as a result of piezoelectrical effect, starting from an arbitrary equilibrium state at the molecular area $A=A_i$ by monolayer compression. It should be noted here that the study of nonequilibrium phenomena in monolayers on a water surface due to the external compression stimulation with an aid of movable barriers requires the consideration of surface pressure propagation in the monolayers (see Fig. 1). However, this leads to a complicated calculation which is very difficult to solve. Therefore we assume here for simplicity that the response of the surface pressure propagation is quicker than that of the dielectric relaxation of monolayers. In this case, for all molecules on a water surface, V is given by

$$V=W_{\text{int}}+RU(A_i-A). \tag{10}$$

It should be noted here that molecular area A decreases along with monolayer compression. W_{int} is the dipole-dipole interaction form function excluding the angular portion, R is the interaction produced as a result of piezoelectric effect, and $U(A_i-A)$ is a unit step function defined as

$$U(A_i-A)=\begin{cases}1 & (A_i>A)\\ 0 & (A_i<A).\end{cases}$$

Substituting Eq. (10) into Eq. (3), the possibility flux flow is rewritten as

$$\mathbf{j}=-\left[\frac{kT}{\xi}\frac{\partial\omega}{\partial\theta}+\frac{W_{\text{int}}}{\xi}\sin\theta\omega+\frac{RU(A_i-A)}{\xi}\sin\theta\omega\right]\mathbf{e}_\theta. \tag{11}$$

In the first order approximation, we assume that the external interaction R works as a perturbation to the equilibrium state expressed by Eq. (5). Therefore Eq. (11) is approximately written as

$$\mathbf{j}\approx-\left\{\frac{kT}{\xi}\frac{\partial\omega}{\partial\theta}+\frac{W_{\text{int}}}{\xi}\sin\theta\omega\right\}_{\text{eq}}\mathrm{e}_\theta-\frac{RU(A_c-A)}{\xi}\sin\theta\omega\mathbf{e}_\theta$$
$$=-\frac{RU(A_i-A)}{\xi}\sin\theta\omega\mathbf{e}_\theta. \tag{12}$$

Using the equation above, Eq. (9) is rewritten as

$$\frac{\partial S}{\partial t}=\frac{RU(A_i-A)}{\xi}\int_0^{\theta_A}\sin^2\theta\omega(\theta,t)\sin\theta d\theta$$
$$=\frac{RU(A_i-A)}{\xi}\overline{\sin^2\theta}, \tag{13}$$

where $\overline{\sin^2\theta}$ is the average value of $\sin^2\theta$. As aforementioned, the external force is considered as a perturbation working to the equilibrium state and influences the orientational distribution of dipoles only very slightly. Therefore the value of $\overline{\sin^2\theta}$ in the equilibrium state in the absence of the external compression can be inserted into Eq. (13). That is, $\overline{\sin^2\theta}$ is approximately given by

$$\overline{\sin^2\theta}=\frac{\int_0^{\theta_A}\sin^2\theta\sin\theta d\theta}{\int_0^{\theta_A}\sin\theta d\theta}=\frac{(2+\cos\theta_A)(1-\cos\theta_A)}{3}. \tag{14}$$

Hence from Eqs. (13) and (14) we obtain

$$\frac{\partial S}{\partial t}=\frac{(2+\cos\theta_A)(1-\cos\theta_A)}{3\xi}RU(A_i-A). \tag{15}$$

In addition to the term given in Eq. (15), the total rate of change of S contains a term due to thermal relaxation motion. The thermal motion will tend to restore the orientational distribution of molecules to the equilibrium distribution in the absence of external stimulation. Introducing $1/\tau$ as a proportionality factor, the total rate of change of S is written as

$$\frac{d(S-S_{\text{eq}})}{dt}=-\frac{S-S_{\text{eq}}}{\tau}+\frac{(2+\cos\theta_A)(1-\cos\theta_A)}{3\xi}$$
$$\times RU(A_i-A), \tag{16}$$

where τ is the relaxation time. This is the equation describing the transient behavior of the monolayer, that is, the dielectric relaxation phenomena in monolayers by monolayer compression. In the following, we discuss the dielectric relaxation phenomena of monolayers in the mean field approximation by solving Eq. (16). Before going to the discussion, we briefly discuss here S_{eq} and R in Eq. (16).

The monolayer mainly experiences a molecule-molecule interaction W_e when the molecular area A is smaller than A_c, that is, shortly after A_c by monolayer compression. The external stimulation to a monolayer is expressed by introducing a step interaction R starting from the molecular area $A=A_i$ close to A_c $(A_i<A_c)$. The orientational order parameter S in the equilibrium state $(=S_{\text{eq}}^e)$ at the molecular area A is expressible in a mean field approximation [11]

$$S_{\text{eq}}^e=\frac{e^t-\cos\theta_A e^{t\cos\theta_A}}{e^t-e^{t\cos\theta_A}}-\frac{1}{t}, \tag{17}$$

where

$$t=\frac{-\mu\langle E_i\rangle}{kT}.$$

Here, $\langle E_i\rangle$ is the average internal electric field acting on the constituent rodlike polar molecules. As calculated in our previous paper [11], the final state satisfies the following relation:

$$S^F-S_{\text{eq}}^e=\frac{R}{12kT}(1-\cos\theta_A)^2, \tag{18}$$

when $|t|\ll 1$ and $|R/kT|\ll 1$. At the equilibrium state, the relation $d(S-S_{\text{eq}}^e)/dt=0$ is satisfied. Therefore from Eqs. (16) and (18), we obtain

$$\frac{R}{12kT}(1-\cos\theta_A)^2=\frac{\tau(2+\cos\theta_A)(1-\cos\theta_A)}{3\xi}R. \tag{19}$$

Hence relaxation time τ becomes

$$\tau^e=\frac{\xi}{4kT}\frac{1-\cos\theta_A}{2+\cos\theta_A}, \tag{20}$$

which is inversely proportional to the diffusion coefficient defined as [12]

$$D=\frac{kT}{\xi}. \tag{21}$$

It is interesting here to note that the relaxation time τ depends on $\cos\theta_A=\sqrt{1-A/A_c}$, thus the relaxation time τ decreases as the molecular area A decreases by monolayer compression. Substituting Eqs. (20) and (21) into Eq. (16), we obtain a differential equation expressing the deviation of the orientational order parameter from the equilibrium state

$$\frac{d\Delta S}{dt}=-\frac{4kT}{\xi}\frac{2+\cos\theta_A}{1-\cos\theta_A}\Delta S+\frac{(2+\cos\theta_A)(1-\cos\theta_A)}{3\xi}RU(A_i-A), \tag{22}$$

where $\Delta S=S-S^e_{\rm eq}$. With the relation $\sin\theta_A=\sqrt{A/A_c}$, we obtain

$$\frac{d(S-S^e_{\rm eq})}{dA}\frac{dA}{dt}=-\frac{4kT(2+\sqrt{1-[A/A_c]})}{\xi(1-\sqrt{1-[A/A_c]})}(S-s^e_{\rm eq})+\frac{(2+\sqrt{1-[A/A_c]})(1-\sqrt{1-[A/A_c]})}{3\xi}RU(A_i-A). \tag{23}$$

In order to analyze the dielectric relaxation phenomena starting from the equilibrium state at the molecular area $A=A_i$ close to A_c $(>A_i)$ by monolayer compression, we approximate Eq. (23) with Eq. (24) which is written as

$$\alpha\frac{d(S-S^e_{\rm eq})}{dA}=\frac{4kT}{\xi}(2+3\sqrt{1-[A/A_c]})\,(S-S^e_{\rm eq})-\frac{RU(A_i-A)}{3\xi}(2-\sqrt{1-[A/A_c]}), \tag{24}$$

with $dA/dt=-\alpha$, where α is the molecule compression speed. When there is no external stimulation, i.e., $R=0$, $\alpha=0$, Eq. (24) returns to the equilibrium equation $S-S^e_{\rm eq}=0$. Here it should be noted that the external interaction R is produced as a result of the constant molecule compression at a speed of α. Integrating the differential equation above from the equilibrium state at $A=A_i$ to a nonequilibrium state at $A=A$ with the initial condition

$$S|_{A=A_i}=S^e_{\rm eq}|_{A=A_i}, \tag{25}$$

we obtain the deviation of order parameter from equilibrium state

$$S-S^e_{\rm eq}|_{A=A}=-\frac{2RA_i}{3\xi\alpha}\left(1-\frac{A}{A_i}\right)\left(1-\frac{A_i-A}{\tau_i}\frac{1}{\alpha}\right)-(S^e_{\rm eq}|_{A=A}-S^e_{\rm eq}|_{A=A_i}). \tag{26}$$

Here τ_i is the value of τ at the molecular area $A=A_i$

$$\tau_i\approx\tau_c=\frac{\xi}{8kT}.$$

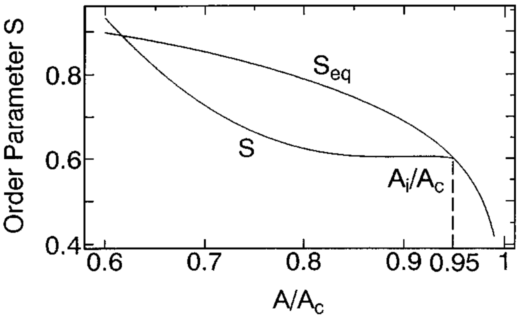

FIG. 2. The nonequilibrium deviation of order parameter S under an external step stimulation when $A_i/\tau_i\alpha=3$, $RA_i/\xi\alpha=3$, and $A_i/A_0=0.95$.

It is obvious from Eq. (26) that the deviation from equilibrium state comes from a step external compression stimulation and that the thermal diffusion effect which is expressed as $(A_i-A)/\tau_i$ tends to bring molecules back to a new equilibrium state $S^e_{\rm eq}|_{A=A}$.

Figure 2 shows an example of the orientational order parameter S when an external step stimulation is applied at the molecule area $A=A_i$, which is calculated from Eq. (26) for $A_i/\tau_i\alpha=3$, $RA_i/\xi\alpha=3$, and $A_i/A_0=0.95$. As will be shown in Fig. 3(b), our experiment gives the results that $S-S_{\rm eq}>0$ is satisfied in the region of molecule area 65 $Å^2<A<95$ $Å^2=A_0$, whereas $S-S^e_{\rm eq}<0$ is satisfied in the region $A<65$ $Å^2$. In other words, the relation $S-S^e_{\rm eq}=0$ is satisfied at the molecule area close to $A=A_0$ and $A=\frac{2}{3}A_0$. Therefore, in the calculation, looking at the first term of Eq. (26), we chose the above parameters as an example. As we can see in Fig. 2, at the initial state, the molecule compression velocity α is greater than $(A_i-A)/\tau$, thus the relation $S-S^e_{\rm eq}<0$ is satisfied. This means that the response of molecules is relatively slow. While the monolayer is further compressed, the molecule compression speed α becomes smaller than $(A_i-A)/\tau$ because the relaxation time decreases as the monolayer is compressed, as aforementioned. Thus the returning speed to the equilibrium state is so quick that molecules cannot stop at the equilibrium state, which leads to $S-S^e_{\rm eq}>0$. From Eq. (26), the deviation of Maxwell displacement current ΔI from the current $I_{\rm eq}$ which flows so as to satisfy the thermodynamic equilibrium condition is expressible as

$$\Delta I=I-I_{\rm eq}=-\frac{16\mu R}{3\xi LA^2}\left(1-\frac{A_i-A}{\tau_c}\frac{1}{\alpha}\frac{A_i+A}{A_i}\right) \tag{27}$$

by substituting Eq. (26) into the following equations:

$$I=\frac{B\alpha\mu}{L}\left(\frac{S}{A^2}-\frac{dS}{AdA}\right), \tag{28}$$

and

$$I_{\rm eq}=\frac{B\alpha\mu}{L}\left(\frac{S^e_{\rm eq}}{A^2}-\frac{dS^e_{\rm eq}}{AdA}\right), \tag{29}$$

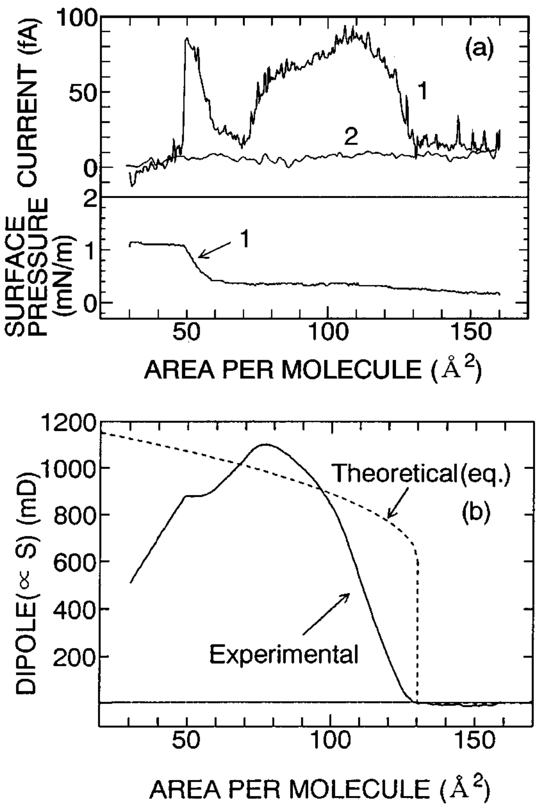

FIG. 3. (a) Experimental Maxwell-displacement current of 5CB with a compression speed of $\alpha=0.054$ Å²/sec. Surface-pressure–area isotherm and Maxwell-displacement-current–area isotherm (from bottom to top). With monolayers on a water surface (curve 1), and without monolayers on a water surface (curve 2). (b) Experimental mean vertical component of dipole moment of 5CB and theoretical mean vertical component of dipole moment at equilibrium.

which were derived in our previous paper [10]. Here B is the working area of electrodes and L the distance between electrode 1 and the water surface (see Fig. 1).

IV. EXPERIMENT

Based on the above discussion, we experimentally investigated the Maxwell displacement current (MDC) across 5CB monolayers on a water surface at the critical molecular area A_c by monolayer compression, and examined the change of the orientational order parameter S with respect to molecular area A. Briefly, the experiment was performed using the experimental system shown in Fig. 1 in a manner similar to that in our previous study [14]. The trough has a rectangular shape with an area of 1050 cm². At the center of the trough, electrode 1 with a working area B of 44.2 cm² was placed parallel to and at a distance L of 1.0 ± 0.05 mm above the water surface. The two electrodes were short circuited with a picoampere electrometer. The generation of MDC was monitored together with the surface pressure-area ($\Pi-A$) isotherm during monolayer compression. The experiment was carried out with a molecule compression speed α of 0.054 Å² sec^{-1}/molecule, with the help of two moving barriers (see Fig. 1) by moving them at a velocity of 30 mm/min [14]. Therefore, the molecules spread on the water surface between the two moving barriers were compressed at a molecule speed α of 0.054 Å² sec^{-1}/molecule. Figure 3(a) gives the results obtained in our experiment and plotted as curve 1 in the figure. From bottom to top, $\Pi-A$ isotherm and MDC area $(I-A)$ isotherm are shown. In the molecular area $A>70$ Å², although the surface pressure is very small, the MDC is clearly generated in a manner as discussed in our previous study [14]. In the figure, $I-A$ isotherm is plotted as curve 2 when no monolayer is formed on a water surface. In this case surface pressure was nearly zero during two barriers were moved (not shown here). As we can see in the figure, MDC is initiated to flow at the critical area A_c of 130 Å² by monolayer compression. The orientational order parameter S, which is proportional to the mean vertical component of dipole moment of molecules $m_z=S\mu$, was calculated from the amount of charge flowing across monolayers, in the same manner as described in our previous study [8], and the results were plotted in Fig. 3(b). Briefly the results were obtained by integrating the MDC in the range between A_0 to A, and then divided it by A, that is

$$m_z=\int_{A_0}^{A} IdA/A\alpha. \tag{30}$$

In Fig. 3(b) the orientational order parameter S^e_{eq} in the equilibrium state is also plotted as a dashed line. As we can find in the figure, our experimental results satisfy the relation $\Delta S<0$ at the molecular area A close to A_c (=130 Å). These results indicate that the barrier velocity $\alpha=-dA/dt$ is large comparing to the response effect $(A_i-A)/\tau_c$ at the transition.

V. DISCUSSION

From the Debye-Brownian equation, we have derived a nonequilibrium dynamic equation of Eq. (16) for the analysis of the dielectric relaxation phenomena of monolayers on a water surface. We expect that this equation is suitable for the analysis of monolayers on a water surface so long as the rodlike polar molecule model is applicable. Expression of the relaxation time given by Eq. (20) was also obtained, and we found that the dielectric relaxation depends on the molecular area A. The order parameter under the mean field approximation was given by Eq. (26). Any monolayer under an external stimulation will exhibit transient behavior, i.e., experience nonequilibrium intermediate states and finally return to a new equilibrium state. The effect of going back to the new equilibrium state is due to the intermolecule energy exchange which is intermolecular diffusion expressed as kT/ξ in Eq. (21). This dielectric relaxation phenomenon gives an additional orientational order parameter ΔS written by Eq. (26) to the equilibrium one S_{eq}. It is also reasonable that the relaxation time τ is inversely proportional to the diffusion coefficient D and depends on the maximum angle θ_A of molecules. Shortly after the onset of transition during monolayer compression, the deviation of order parameter S from S^e_{eq} at the equilibrium state is decided by the balance between the compression speed α and the relaxation time τ at the molecule area A close to A_c. As shown in Fig. 3(b), at the beginning of the transition, the compression speed is relatively large comparing to the response effect

$[\alpha > (A_i - A)/\tau_c]$. Thus the molecules retard to react to such a rapid external change and results in $\Delta S < 0$. After the onset of the transition, the response effect suppresses the compression effect, that is, $\alpha < (A_i - A)/\tau_c$. Thus returning to the equilibrium state cannot completely stop due to the inertia effect. This leads to $\Delta S > 0$ at some stages after the onset of transition. In Fig. 3(b), $S > S^e_{\mathrm{eq}}$ is satisfied in the region 65 $\text{Å}^2 < A < 95\ \text{Å}^2$.

The present calculation also reveals the whole relaxation process under the external compression stimulation starting from the molecule area A_i near the critical molecular area A_c. As the monolayer is compressed by an external step stimulation from A_i, the deviation of order parameter S from the order parameter S^e_{eq} at the equilibrium state becomes larger, which means that the nonequilibrium effect cannot be negligible. The returning of nonequilibrium states to equilibrium states happens after the deviation of the order parameter reaches the maximum. The returning speed depends on the balance between the speed of compression α and the relaxation speed which is related to the friction constant ξ of monolayer. For a further understanding of the dielectric relaxation phenomena, we need to clarify the piezoelectrical effect represented by R. However, this is a future task. Further theoretical calculation is being proceeded. It is instructive here to point out that the relaxation time and viscosity of Langmüir film can be examined hereafter on the basis of the Maxwell displacement current measurement and the analysis developed here.

VI. CONCLUSION

The dielectric relaxation phenomena of organic monolayers on a water surface under the external compression were investigated on the basis of rotational Debye-Brownian equation. The effect of relaxation, which is obtained as Eqs. (20) and (22), generates a deviation of order parameter ΔS from that of equilibrium state. The nonequilibrium dielectric relaxation process depends on the balance between the barrier velocity α and the response speed defined as $(A_i - A)/\tau_c$. It was found that the relation $\Delta S < 0$ is satisfied at the onset of transition in the case of the Maxwell displacement current measurement of 5 CB monolayers performed in the present experiment.

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