Electro-optic response of a ferroelectric liquid crystal in thick free-standing films

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We study the electro-optic response of a ferroelectric liquid crystal in free-standing films as thick as the helical pitch. In the films thicker than about one pitch, two relaxation modes are observed in the frequency spectra. The relaxation frequency of the slower mode decreases when increasing the film thickness, while that of the faster mode, which appears at approximately 1 kHz, is almost independent of the film thickness. In thinner films, a single relaxation mode is observed at several hundred Hz. The obtained relaxation spectra are discussed in comparison to the theoretical spectra of the phase mode in a system of finite length along the helical axis calculated by Urbanc and Žekš [Phys. Rev. E **52**, 3892 (1995)].

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Free-standing films of smectic liquid crystals have attracted much attention from researchers because they offer an experimentally available quasi-two-dimensional system [1]. The effect of the confined dimension on the structure and the dynamic properties of liquid crystals can be studied by varying the thickness of a film from only two, to thousands of smectic layers. In a very thin film where liquid crystals are self-confined in quasi-two-dimensions, the behavior at phase transition [2–5] and the material properties such as elastic constant and viscosity [5–7] are found to depend strongly upon the film thickness. By increasing the film thickness, one can also observe the crossover from surface-dominant (two-dimensional) behavior to bulk-dominant (three-dimensional) behavior.

In the chiral ferroelectric smectic-*C* (Sm-*C**) phase, the molecules are arranged into layers and their long axes (directors) are tilted with respect to the layer normal. The molecular tilt rotates around the layer normal due to the chirality of the molecules. The spontaneous polarization lies in the plane of the smectic layer and is perpendicular to the director. In a free-standing film of ferroelectric liquid crystal (FLC), the smectic layers stack parallel to the surfaces of the film and the helical axis is perpendicular to them.

The dynamic response of FLC's to an electric field has also been studied intensively in free-standing films [8–11]. When a strong ac electric field is applied parallel to the layers, the directors switch between two stable directions due to the ferroelectric coupling between the spontaneous polarization and the electric field. Recently, Uto *et al.* [11] reported the switching behavior of an electro-optic response without threshold voltage and hysteresis in free-standing films. They also reported that the switching time in the films is much shorter than that in a surface-stabilized cell. Such significant changes of switching behavior are interpreted by the strong influence of the glass substrates on the dynamics of FLC's in cells. Therefore, a thick, free-standing film seems to be suitable for the study of the intrinsic bulk properties of FLC's without the restriction of cell surfaces.

Under a small electric field, two corrective relaxation modes of directors are reported in the Sm-*C** phase of bulk FLC's [12]. One is the soft (amplitude) mode, which is the fluctuation in the magnitude of the tilt angle. The other is the Goldstone (phase) mode, which is the fluctuation in the azimuthal angle of directors around the helical axis. Except in the vicinity of the Smectic-*A* (Sm-*A*) to Sm-*C** phase transition, the contribution of the Goldstone mode is predominant in the dielectric and electro-optic responses.

In most studies on the dynamics of the phase mode of FLC's, a sample is aligned in a sandwich cell as the helical axis is parallel to the cell surfaces. Therefore, the size of the system along the helical axis is infinitely large compared to the helical pitch. In this paper, we regard a thick, free-standing film of FLC's as a system of finite length along the helical axis and study the dynamics of the phase mode in these films by examining the electro-optic response to a small sinusoidal electric field. Both the dielectric and electro-optic responses have been utilized to study the dynamics of FLC's in sandwich cells and they offer equivalent information on the phase mode. However, the dielectric measurement in free-standing films is difficult because of their small capacitance due to the large separation between electrodes and the small electrode area. In contrast, the electro-optic response is not seriously influenced by the size of a film or its dc conductivity. Therefore, the electro-optic method is employed to study the dynamics of the phase mode in this study. The obtained frequency dependence of the electro-optic response has been discussed by the theoretical spectrum of the permittivity for the phase mode of FLC's in a finite-size system along the helical axis.

The FLC used in this study was *p*-decyloxy-benzylidene-*p'*-amino-2-methylbuthylcinnamate (DOBAMBC). We prepared a free-standing film by drawing the liquid crystal over a 1×5 mm^2 rectangular slit in the Sm-*A* phase. The longer sides of the slit are made of brass to enable the application of an electric field parallel to the smectic layers. We determined the film thickness by ellipsometry in the polarizer-compensator (quarter-wave plate)-sample-analyzer configuration using the fixed compensator nulling method in the Sm-*A* phase [4,5]. Subsequently, the film was cooled to the Sm-*C** phase and we measured the frequency dependence of the electro-optic response at 4 °C below the Sm-*A*–Sm-*C** phase transition temperature. Although the transition temperature T_c strongly depends on the film thickness in thin free-standing films [3–5], the films we studied are so thick that they might be in the same condition at the same temperature.

A sinusoidal electric field of 0.4 V/mm was applied to the films and is sufficiently small not to trigger the switching of directors in glass cells. The electro-optic response is in the linear regime, judging from the negligibly small magnitude of the harmonic components. We also applied a small dc bias electric field of 2 V/mm to suppress the rigid rotation of the directors as a whole. Although the magnitude of a dc bias field is sufficiently small not to change the helical pitch, it renders the direction of the total polarization of the film $\vec{p}$ parallel to the field and that of the optical axis perpendicular to the field.

In a homeotropically aligned FLC film, which is illuminated from the oblique direction to the smectic layer normal, the electro-optic response is mainly due to the change of the birefringence δn induced by the applied electric field, as long as the change of the pitch and that of the optical axis are negligible. When the tilt angle is small and the respective smectic layers are approximately optically uniaxial, the induced birefringence δn in a free-standing film illuminated obliquely at 45° to the film normal is proportional to the change of $\langle \cos\phi \rangle$, $\delta n \propto \delta \langle \cos\phi \rangle$, where ϕ is the azimuthal angle of the director and $\langle \cdots \rangle$ represents the spatial average over the film. On the other hand, the field-induced polarization δP concerning the phase mode is also proportional to $\delta \langle \cos\phi \rangle$. Therefore, the electro-optic response is approximately proportional to the permittivity and it is possible to obtain equivalent information on the dynamics of the phase mode from the linear electro-optic measurement.

The optical setup of the electro-optic measurement is the same as that for ellipsometry. The beam of a He-Ne laser ($\lambda = 632.8$ nm) is perpendicular to the applied electric field and incident on a film under an angle of 45° to detect the response of the phase mode. The compensator is fixed at an angle of 45° with respect to the plane of incidence. The polarizer and the analyzer are set to the angle at which the intensity of the transmitted light after passing through the analyzer becomes minimum in the Sm-A phase. By this adjustment, we can reduce the dc component of the transmitted light due to the static part of the birefringence and make the measurement more sensitive to the ac component in the electro-optic response.

The intensity of the transmitted light after passing through the analyzer was detected by a photodiode, and the magnitude and the phase shift of the fundamental frequency component was measured by a fast Fourier transform (FFT) analyzer. After the electro-optic measurement, we heat the film to the Sm-A phase again and check that the film thickness has not changed during the measurement.

The frequency dependence of the electro-optic response has been studied in free-standing films by varying their thickness from approximately 200 to 2400 layers. It is found that the obtained spectra can be classified into three types by the number of apparent relaxation modes. In the films thicker than approximately 1000 layers, two relaxation modes appear in the spectrum. The complex spectrum of the transmitted light intensity I^* $(\equiv I' - iI'')$ obtained in the films of 2350 ± 30 layers and 1165 ± 30 layers are shown in Figs. 1(a) and 1(b), respectively. By varying the film thickness, it is found that the relaxation frequency of the lower frequency

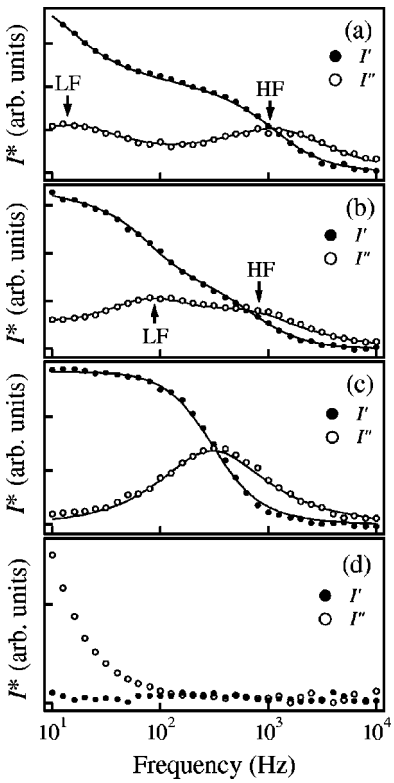

FIG. 1. Complex spectrum of the transmitted light intensity I^* $(\equiv I' - iI'')$ obtained for free-standing films of DOBAMBC. (a) 2350 ± 30 layers, (b) 1165 ± 30 layers, (c) 660 ± 30 layers, (d) 211 ± 10 layers. Solid lines in (a)–(c) are the best-fitted curves of Eqs. (1) and (2).

mode (LF mode) decreases with increasing the film thickness, while that of the higher frequency mode (HF mode) which appears at about 1 kHz is almost independent of the film thickness. In the films thinner than approximately 1000 layers, only one relaxation mode is observed in the spectrum. The spectrum obtained in the film of 660 ± 30 layers is shown in Fig. 1(c). In a film belonging to this type, the relaxation frequency increases slightly with decreasing the thickness of the film. Furthermore, no relaxation mode is apparent in the film of 211 ± 10 layers, as shown in Fig. 1(d). The imaginary part I'' monotonically increases as the frequency decreases and the real part I' is much smaller than I'' in this film.

Except for the film of 211 ± 10 layers, the observed electro-optic responses exhibit the Debye-type relaxation behavior. This is different from the frequency dependence of the scattered light intensity in free-standing films of a FLC with high spontaneous polarization under a high electric field reported by Demikhov *et al.* [9]. They observed a resonance-type frequency spectrum due to the switching of directors accompanied by the movement of a kink through the film where the FLC molecules are uniformly aligned. However, the applied electric field is much smaller in our experiment and the observed relaxation is attributed to the fluctuation of the helical structure, which is the same as that observed in thick cells. In a thick homogenous cell where the smectic layers are arranged perpendicular to the surfaces of the cell, the relaxation of permittivity due to the Goldstone mode is

observed at 400 Hz for DOBAMBC [13]. We assign the HF mode to the Goldstone mode observed in cells according to its relaxation frequency and its independence of the film thickness. On the other hand, in a thin surface-stabilized homogeneous cell where the helical structure is unwound by the surface anchoring, a relaxation mode whose relaxation frequency depends on the cell thickness has been observed by electro-optic [14,15] and dielectric measurement [16]. This mode is attributed to the twisted structure of molecules along the direction perpendicular to the cell surfaces. However, we cannot assign the LF mode to this mode because the corresponding size in a free-standing film is independent of the film thickness. From the thickness dependence of the relaxation frequency, it is evident that the LF mode corresponds to the fluctuation of the azimuthal angle (phase mode) confined in a film of finite length.

Recently, Kutnjak-Urbanc and Žekš studied the dynamics of the phase mode of FLC's in a system of finite length along the helical axis theoretically [17]. They calculated the dielectric response in a finite system by the Landau-Khalatnikov equation for the azimuthal angle and found the relaxation mode that satisfies the free boundary condition other than the Goldstone mode. This mode relates the unwinding motion of the whole helical structure and its relaxation time depends on the system size L. When a small sinusoidal electric field with an angular frequency ω, $\delta\vec{E}=\delta\vec{E}_0\cos(\omega t)$, is applied parallel to the total polarization of the system $\vec{p}$ $(\delta\vec{E}\|\vec{p})$, the real χ' and the imaginary part χ'' of the permittivity χ^* are respectively given as

$$\chi'=\frac{P_s l^4}{2E_c}\cos^2\left(\frac{\pi l}{2}\right)\times\sum_{k=0}^{\infty}\frac{(2k+1)^2}{[(2k+1)^4+l^4\Omega^2][(2k+1)^2-l^2]^2}, \quad (1)$$

$$\chi''=\frac{P_s l^6}{2E_c}\cos^2\left(\frac{\pi l}{2}\right)\times\sum_{k=0}^{\infty}\frac{\Omega}{[(2k+1)^4+l^4\Omega^2][(2k+1)^2-l^2]^2}, \quad (2)$$

where E_c is the critical electric field to unwind the helical structure, P_s is the spontaneous polarization, $l=2L/p$ is the dimensionless length of the system scaled by the helical pitch p and $\Omega=\gamma\omega/K_3q_0^2$ (γ is the rotational viscosity, K_3 is the elastic constant, and q_0 is the wave number of the helix) is the dimensionless frequency. The theoretical spectrum of χ^* is written as the sum of the stationary waves that satisfy the free boundary condition. The relaxation frequency of the slowest mode $(k=0)$ with the longest wavelength is $f_0=\pi K_3/2\gamma L^2$. Since the magnitude of the higher harmonic modes decreases rapidly with the order k, the contribution of the slowest mode $(k=0)$ is predominant in the measured spectrum. We can observe this mode within the available frequency range in a free-standing film whose thickness is only a few times as long as the helical pitch. However, in sandwich cells, the size of the system along the helical axis L is so large that the relaxation frequency f_0 becomes very low and one cannot observe it within the practical frequency range of the measurement.

According to Eqs. (1) and (2), the higher harmonic mode whose relaxation frequency is nearest to that of the Goldstone mode also makes a large contribution to the spectrum compared to the other harmonic modes. This is the reason why there are two apparent relaxation modes in the spectrum of a thick free-standing film and we can assign the HF mode observed in the thick films to this higher harmonic mode closest to the Goldstone mode. As the thickness of a film increases, the frequency of the HF mode approaches that of the Goldstone mode and becomes insensitive to the variation of the film thickness. Therefore, the HF and LF modes seem to be independent in thick films, though they are related in terms of their origin. In contrast, the LF mode approaches the HF mode as the thickness of a film decreases. They finally merge into one mode for films thinner than approximately $1.5p$ and the relaxation frequency of this mode depends on the film thickness. This is the reason why only one relaxation mode whose relaxation frequency is lower than that of the Goldstone mode is observed in films thinner than approximately 1000 layers.

We attempted to fit the obtained frequency dependence of the electro-optic response with the sum of the two Debye-type relaxation spectra, but it does not fit well to the data in the middle frequency range between the two modes. On the other hand, the measured spectra not only with two peaks in I'' but also with a single peak can be analyzed well by Eqs. (1) and (2). The solid lines in Figs. 1(a)–1(c) are the best-fitted curves of Eqs. (1) and (2) with the increment, L/p, and the relaxation time of the Goldstone mode, $\tau\equiv\gamma/K_3q_0^2$, as fitting parameters. In the film of 211 ± 10 layers, there is no relaxation in the spectrum and we cannot explain it by Eqs. (1) and (2). As the frequency of the slowest mode f_0 exceeds

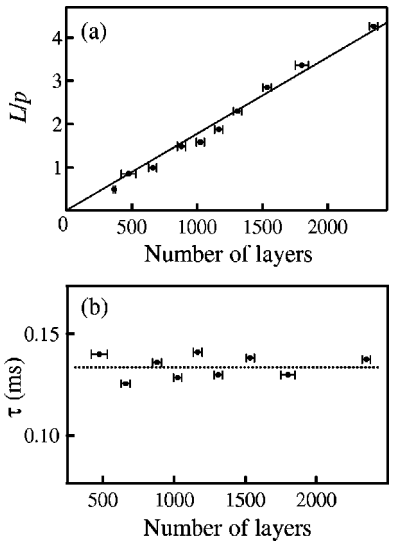

FIG. 2. Dependence of the best-fitted values of (a) the ratio L/p and (b) the relaxation time τ on the number of layers. The solid line in (a) represents the best-fit line to the data. The dotted line in (b) represents the average value of τ, 0.33 ms.

that of the Goldstone mode in such a thin film, the contribution of the size-dependent phase mode tends to be suppressed. The spectrum at low frequencies shown in Fig. 1(d) might be due to the rigid rotation of directors induced by the switching of the total polarization $\vec{p}$ even under a small dc bias field in thin films. A more detailed study is necessary to conclude whether the relaxation behavior disappears or is only suppressed in thin films and to examine the influence of the dc bias field.

The dependence of the best-fitted values of L/p and τ on the film thickness are shown in Figs. 2(a) and 2(b), respectively. We find the linear relationship between L/p and the number of layers. From the slope of the best-fitted line in Fig. 2(a), the pitch p is found to correspond to 564 layers. By using the reported values of the pitch $p=2.2$ μm, the layer thickness in the Sm-A phase $d=3.33$ nm and the tilt angle $\theta=18°$ at 4 °C below T_c for DOBAMBC in a sandwich cell [13], one pitch is found to correspond to 695 layers. This discrepancy indicates that the helical structure tends to unwind in sandwich cells and the pitch is elongated by the influence of the cell surfaces. The relaxation time of the Goldstone mode τ is found to be approximately 0.13 ms and is almost independent of the film thickness except that in 365 ± 10 layers. This value of τ is threefold smaller than that obtained by the dielectric measurement in a sandwich cell [13]. The short relaxation time in a free-standing film is partly due to the small value of the pitch p, as mentioned above. The relaxation time τ in the film of 365 ± 10 layers is 0.35 ms and is much longer than those of other films. However, it is difficult to obtain the appropriate values of τ and L/p for the spectrum with a single relaxation mode because these parameters are not independent of each other. If the value of τ is fixed to the average value of 0.13 ms, the spectrum can be well fit with $L/p=0.77$. Therefore, the discrepancy of τ in this film is only due to the artifact from the fitting procedure.

In conclusion, we study the dynamics of the phase mode of FLC's in thick free-standing films by examining the electro-optic response. The obtained electro-optic spectra are found to have good agreement with the theoretical spectra of permittivity predicted for a finite-size system along the helical axis by Kutnjak-Urbanc and Žekš. Both the relaxation time of the Goldstone mode and the helical pitch are slightly shorter than those reported in sandwich cells. These differences are partly due to the influence of the glass substrates in cells.

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