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# Study on the Surface Alignment of Nematic Liquid Crystals: Determination of the Easy Axis and Temperature Dependence of its Field Energy

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The assumption which was described in the previous paper<sup>1</sup> has been proven in this paper. Namely, the easy axis is determined by means of the van der Waals forces for the free surface of liquid crystals and for the interface between a liquid crystal and an anisotropic solid surface. The energy of the easy axis is discussed and it is proven that this energy varies as the surface order parameter with temperature.

#### **INTRODUCTION**

The problem of why liquid crystals (LC) align on a treated solid surface has been studied from various approaches. They are roughly classified into following four kinds:

- 1) Topographical or geometrical structures of a treated solid surface cause an alignment of LC molecules.<sup>2-9</sup> This is based on minimization of bulk deformation energy in the LC phase. From a macroscopic point of view, this approach is very reasonable. Actually, it seems partially be successful.
- 2) Physico-chemical interactions occur at the interface between the LC and the treated surface. This approach is useful especially for a surface coated with an organic surfactant. The relationship between the alignment and the surface tension was also explained. Recently, an interaction of the polar part is discussed. But for the free surface of the LC, it may be difficult to describe the surface alignment.

- 3) Another influential interaction is in terms of the van der Waals forces.<sup>20-25</sup> Many significant problems at the surface had been explained from this approach.
  - 4) Other approaches have been investigated. 26,27

On the other hand, the temperature dependence of the pretilt angle is a remarkable surface phenomena. This fact had been observed experimentally for the free surface of p-azoxyanisole (PAA) and p-methoxybenzylidene-n-butyl aniline (MBBA)<sup>28,29</sup> and for the LC-solid interface.<sup>30,31</sup> Taking into account this fact, those analyses mentioned above cannot completely explain both the pretilted alignment and the temperature dependence of pretilt angles for the free surface and the interface with a solid.

In the previous paper, the author described the temperature dependence of pretilt angles theoretically not only for the free surface of PAA and MBBA but also for the interface between a treated solid and the biphenyl LC using the concept of the easy axis field. The easy axis (EA) was defined in that paper by the direction of the director when minimum energy of the van der Waals forces between the LC and the phase in contact with it was realized. The contact phase with the LC can be taken with an arbitrary material. It should be noted that the director is not necessary to align with its direction along the easy axis. The pretilted alignment comes from the balance between the bulk and the surface energies which are expanded by means of the bulk order O and the surface order  $\overline{\mathbf{Q}}$ , respectively. The surface energy contains the energy of the EA field which had been expressed by the formulation of  $-\Delta \pi \{(\mathbf{n} \cdot \mathbf{d})^2\}$ -1/3/2, where **n** and **d** are the director of the LC and the EA, respectively. The constant  $\Delta \pi$  shows the anisotropy of alignment constant. Moreover in that paper, it was assumed that the EA is normal or parallel to the surface and  $\Delta \pi$  varies with temperature as the order parameter S. These assumptions are, however, not so clear facts.

Therefore in this paper, proof will be presented for these assumptions, i.e. the EA is determined for the free surface; the case that the optical axis of the solid is arbitrarily tilted to the surface; and the fact that the EA field energy depends on S with temperature. Furthermore, the solutions of the pretilt angle were degenerated to  $\pm \theta_0$  in the previous paper. This is in contradiction with empirical fact, and will be briefly discussed.

# II ENERGY BETWEEN TWO ANISOTROPIC BODIES

In order to determine the EA, an interaction energy between two bodies must be estimated in terms of the van der Waals forces. Other types of interaction must also be considered, such as molecular dipole and so on. However, the

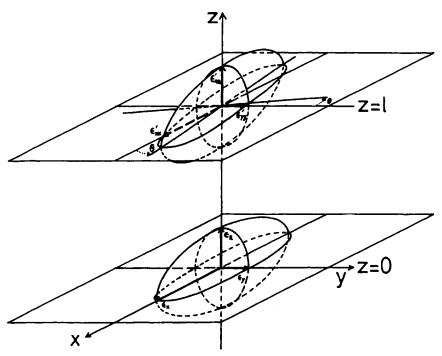


FIGURE 1 Relation between the coordinate system and dielectric permiabilities. The principal axis is rotated by  $\theta$  about the z-axis.

dispersion forces may dominant in the case of the LC and glass materials. Thus, we restrict our attention to the van der Waals forces.

The van der Waals forces acting between two anisotropic bodies were calculated by several authors. 20,21,32,33 A more general formulation was derived by Kihara and Honda<sup>34</sup> in the case where the dielectric permeabilities of two bodies have an uniaxial anisotropy. The nematic LC is an uniaxial state, however, there is no evidence that the treated solid surface is uniaxial. Then we must consider the biaxial case generally. Furthermore, a few authors 22,24,35 discussed the energy when one of the bodies is rotated arbitrarily about the normal axis to the surface. In this situation (see Figure 1), the dielectric permeabilities of two bodies can be expressed as

$$\boldsymbol{\varepsilon}' = \begin{pmatrix} \varepsilon_{\mathbf{x}}' & 0 & 0 \\ 0 & \varepsilon_{\mathbf{y}}' & 0 \\ 0 & 0 & \varepsilon_{\mathbf{z}}' \end{pmatrix}, \qquad \boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_{\mathbf{x}\mathbf{x}} & \varepsilon_{\mathbf{x}\mathbf{y}} & 0 \\ \varepsilon_{\mathbf{x}\mathbf{y}} & \varepsilon_{\mathbf{y}\mathbf{y}} & 0 \\ 0 & 0 & \varepsilon_{\mathbf{z}\mathbf{z}} \end{pmatrix}, \tag{1}$$

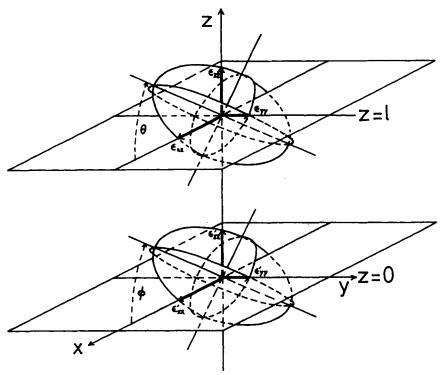


FIGURE 2 The coordinate system and dielectric permiabilities. The principal axis of the solid body is tilted by  $\phi$ .

and the energy is as follows.

$$U_{z}(l) = -\frac{\hbar k_{c}^{2}}{8\pi^{2}}$$

$$\times \int_{0}^{\infty} \left[ \ln \left\{ 1 - \frac{(\sqrt{\varepsilon_{x}'\varepsilon_{z}'} - 1)(\sqrt{\varepsilon_{zz}}\sqrt{\varepsilon_{xx}} - 2\sqrt{\varepsilon_{xy}\varepsilon_{zz}} - 1)}{(\sqrt{\varepsilon_{x}'\varepsilon_{z}'} + 1)(\sqrt{\varepsilon_{zz}}\sqrt{\varepsilon_{xx}} - 2\sqrt{\varepsilon_{xy}\varepsilon_{zz}} + 1)} \exp(-2lk_{c}) \right\} + \ln \left\{ 1 - \frac{(\sqrt{\varepsilon_{y}'\varepsilon_{z}'} - 1)(\sqrt{\varepsilon_{zz}}\sqrt{\varepsilon_{yy}} - 2\sqrt{\varepsilon_{xy}\varepsilon_{zz}} - 1)}{(\sqrt{\varepsilon_{y}'\varepsilon_{z}'} + 1)(\sqrt{\varepsilon_{zz}}\sqrt{\varepsilon_{yy}} - 2\sqrt{\varepsilon_{xy}\varepsilon_{zz}} + 1)} \exp(-2lk_{c}) \right\} \right] d\omega,$$
(2)

where  $k_c$ , h and l stand for the cut-off wavelength, <sup>25</sup> Planck's constant, and the gap between two bodies, respectively. Similarly, when the dielectric

principal axis of one of bodies tilts to the surface (see Figure 2), the energy can be derived as follows:

$$U_{y}(l) = -\frac{\hbar k_{c}^{2}}{8\pi^{2}}$$

$$\times \int_{0}^{\infty} \left[ \ln \left\{ 1 - \frac{(\sqrt{\varepsilon_{zz}^{\prime}} \sqrt{\varepsilon_{xx}^{\prime}} - 2\sqrt{\varepsilon_{xz}^{\prime}} \varepsilon_{zz}^{\prime}} - 1)(\sqrt{\varepsilon_{zz}} \sqrt{\varepsilon_{xx}} - 2\sqrt{\varepsilon_{xz}^{\prime}} \varepsilon_{zz}^{\prime}} - 1)}{(\sqrt{\varepsilon_{zz}^{\prime}} \sqrt{\varepsilon_{xx}^{\prime}} - 2\sqrt{\varepsilon_{xz}^{\prime}} \varepsilon_{zz}^{\prime}} + 1)(\sqrt{\varepsilon_{zz}} \sqrt{\varepsilon_{xx}} - 2\sqrt{\varepsilon_{xz}^{\prime}} \varepsilon_{zz}^{\prime}} + 1)} \right] + \ln \left\{ 1 - \frac{(\sqrt{\varepsilon_{zz}^{\prime}} \sqrt{\varepsilon_{yy}^{\prime}} - 2\sqrt{\varepsilon_{xz}^{\prime}} \varepsilon_{zz}^{\prime}} - 1)(\sqrt{\varepsilon_{zz}} \sqrt{\varepsilon_{yy}} - 2\sqrt{\varepsilon_{xz}^{\prime}} \varepsilon_{zz}^{\prime}} - 1)}{(\sqrt{\varepsilon_{zz}^{\prime}} \sqrt{\varepsilon_{yy}^{\prime}} - 2\sqrt{\varepsilon_{xz}^{\prime}} \varepsilon_{zz}^{\prime}} + 1)(\sqrt{\varepsilon_{zz}^{\prime}} \sqrt{\varepsilon_{yy}} - 2\sqrt{\varepsilon_{xz}^{\prime}} \varepsilon_{zz}^{\prime}} + 1)} \right\} \right\} d\omega, \quad (3)$$

with the dielectric permeabilities of two bodies of the form

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_{xx} & 0 & \varepsilon_{xz} \\ 0 & \varepsilon_{yy} & 0 \\ \varepsilon_{xz} & 0 & \varepsilon_{zz} \end{pmatrix}, \qquad \boldsymbol{\varepsilon}' = \begin{pmatrix} \varepsilon'_{xx} & 0 & \varepsilon'_{xz} \\ 0 & \varepsilon'_{yy} & 0 \\ \varepsilon'_{xz} & 0 & \varepsilon'_{zz} \end{pmatrix}.$$

As well known, this type of energy can have its meaning where the gap is larger than certain small distance  $l_0$ . This distance  $l_0$  is comparable to  $k_c$ , and is of the order of molecular dimension.<sup>25</sup> Nevertheless, it is possible to consider the plane separated by  $l_0$  from the interface as a new one instead of the true interface. The distance  $l_0$  is very small from a macroscopic point of view, then it may be able to neglect it. Namely, one cannot distinguish the new interface and the true interface separately.

#### III DETERMINATION OF THE EA

From the energy of the van der Waals forces described in the above section, the EA can be determined by minimizing those energies. Here, the EA will be determined for the following two cases; at the free surface of the LC and at the interface between the LC and the anisotropic solid.

#### A Free surface of LC

The energy expressed by Eqs. (2) or (3) has a positive value when two bodies are in contact with each other, and reduce to zero when two bodies are

separated an infinite distance. In the case that two bodies are both LC's, the energy is the bulk energy of the combined LC. Since it is not necessary to consider the case of rotation about the normal axis to the surface, the surface energy of the LC is defined as  $U_y(\infty) - U_y(0) = -U_y(0)$ . Here, let us put  $-U_y(0)$  as  $U^{\text{free}}$  for convenience. Therefore the energy of the free surface can be given by following equation.

$$U^{\text{free}} = \frac{\hbar k_c^2}{8\pi^2} \int_0^{\infty} \ln \left[ \left\{ 1 - \frac{(\sqrt{\varepsilon_{zz}}\sqrt{\varepsilon_{xx} - 2\sqrt{\varepsilon_{xz}\varepsilon_{zz}} - 1)^2}}{(\sqrt{\varepsilon_{zz}}\sqrt{\varepsilon_{xx} - 2\sqrt{\varepsilon_{xz}\varepsilon_{zz}} + 1)^2}} \right\} \times \left\{ 1 - \frac{(\sqrt{\varepsilon_{zz}}\sqrt{\varepsilon_{yy} - 2\sqrt{\varepsilon_{xz}\varepsilon_{zz}} - 1)^2}}{(\sqrt{\varepsilon_{zz}}\sqrt{\varepsilon_{yy} - 2\sqrt{\varepsilon_{xz}\varepsilon_{zz}} + 1)^2}} \right] d\omega$$
 (4)

Minimum  $U^{\text{free}}$  is realized when the inside term of the logarithm is minimized. Here,  $\epsilon$  is given as follows under the conditions that the directors rotate about the y-axis by  $\theta$ , and that  $\phi$  is equal to  $\theta$ ,

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_{\parallel} \sin^2 \theta + \varepsilon_{\perp} \cos^2 \theta & 0 & \Delta \varepsilon \sin \theta \cos \theta \\ 0 & \varepsilon_{\perp} & 0 \\ \Delta \varepsilon \sin \theta \cos \theta & 0 & \varepsilon_{\parallel} \cos^2 \theta + \varepsilon_{\perp} \sin^2 \theta \end{pmatrix}, \tag{5}$$

where  $\varepsilon_{\parallel}$  and  $\varepsilon_{\perp}$  are dielectric permeabilities of the LC parallel and perpendicular to the director, respectively, and  $\Delta\varepsilon$  is  $\varepsilon_{\parallel}-\varepsilon_{\perp}$ . Substituting Eq. (5) into the inside term of the logarithm in Eq. (4) and putting the derivative with respect to  $\theta$  as zero, the energy is minimized when  $\theta=0$  or  $\pi/2$ . The EA is then parallel or perpendicular to the free surface of the LC.

# B Anisotropic solid-LC interface

From Eqs. (2) and (3), the interfacial energies  $U^{\rm int}$  can be given by

$$U_z^{\text{int}} = \frac{\hbar k_c^2}{8\pi^2} \int_0^\infty \ln \left[ \left\{ 1 - \frac{(\sqrt{\varepsilon_x^s \varepsilon_z^s} - 1)(\sqrt{\varepsilon_{zz}} \sqrt{\varepsilon_{xx}} - 2\sqrt{\varepsilon_{xy} \varepsilon_{zz}} - 1)}{(\sqrt{\varepsilon_x^s \varepsilon_z^s} + 1)(\sqrt{\varepsilon_{zz}} \sqrt{\varepsilon_{xx}} - 2\sqrt{\varepsilon_{xy} \varepsilon_{zz}} + 1)} \right\}$$

$$\times \left\{ 1 - \frac{(\sqrt{\varepsilon_y^s \varepsilon_z^s} - 1)(\sqrt{\varepsilon_{zz}} \sqrt{\varepsilon_{yy}} - 2\sqrt{\varepsilon_{xy} \varepsilon_{zz}} - 1)}{(\sqrt{\varepsilon_y^s \varepsilon_z^s} + 1)(\sqrt{\varepsilon_{zz}} \sqrt{\varepsilon_{yy}} - 2\sqrt{\varepsilon_{xy} \varepsilon_{zz}} + 1)} \right\} d\omega, \tag{6}$$

for the case of rotating the LC phase about the z-axis, and

$$U_{y}^{\text{int}} = \frac{\hbar k_{c}^{2}}{8\pi^{2}}$$

$$\times \int_{0}^{\infty} \ln \left[ \left\{ 1 - \frac{(\sqrt{\varepsilon_{zz}^{s}} \sqrt{\varepsilon_{xx}^{s} - 2\sqrt{\varepsilon_{xz}^{s} \varepsilon_{zz}^{s}}} - 1)(\sqrt{\varepsilon_{zz}} \sqrt{\varepsilon_{xx} - 2\sqrt{\varepsilon_{xz} \varepsilon_{zz}}} - 1)}{(\sqrt{\varepsilon_{zz}^{s}} \sqrt{\varepsilon_{xx}^{s} - 2\sqrt{\varepsilon_{xz}^{s} \varepsilon_{zz}^{s}}} + 1)(\sqrt{\varepsilon_{zz}} \sqrt{\varepsilon_{xx} - 2\sqrt{\varepsilon_{xz} \varepsilon_{zz}}} + 1)} \right\}$$

$$\times \left\{ 1 - \frac{(\sqrt{\varepsilon_{zz}^{s}} \sqrt{\varepsilon_{yy}^{s} - 2\sqrt{\varepsilon_{xz}^{s} \varepsilon_{zz}^{s}}} - 1)(\sqrt{\varepsilon_{zz}} \sqrt{\varepsilon_{yy} - 2\sqrt{\varepsilon_{xz} \varepsilon_{zz}}} - 1)}{(\sqrt{\varepsilon_{zz}} \sqrt{\varepsilon_{yy} - 2\sqrt{\varepsilon_{xz} \varepsilon_{zz}}} + 1)} \right\} \right] d\omega,$$

$$(7)$$

for the case that the optical axis of the solid is tilted as shown in Figure 2. The dielectric permeabilities of the LC  $\varepsilon$  and of the solid body  $\varepsilon$  are as follows:

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_{\parallel} \sin^{2} \theta + \varepsilon_{\perp} \cos^{2} \theta & \Delta \varepsilon \sin \theta \cos \theta & 0 \\ \Delta \varepsilon \sin \theta \cos \theta & \varepsilon_{\parallel} \cos^{2} \theta + \varepsilon_{\perp} \sin^{2} \theta & 0 \\ 0 & 0 & \varepsilon_{\perp} \end{pmatrix},$$

$$\boldsymbol{\varepsilon}^{s} = \begin{pmatrix} \varepsilon_{x}^{s} & 0 & 0 \\ 0 & \varepsilon_{y}^{s} & 0 \\ 0 & 0 & \varepsilon_{z}^{s} \end{pmatrix},$$
(8)

for Eq. (6) as shown in Figure 1, and

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_{\parallel} \sin^{2} \theta + \varepsilon_{\perp} \cos^{2} \theta & 0 & \Delta \varepsilon \sin \theta \cos \theta \\ 0 & \varepsilon_{\perp} & 0 \\ \Delta \varepsilon \sin \theta \cos \theta & 0 & \varepsilon_{\parallel} \cos^{2} \theta + \varepsilon_{\perp} \sin^{2} \theta \end{pmatrix},$$

$$\boldsymbol{\varepsilon}^{s} = \begin{pmatrix} \varepsilon_{x}^{s} \sin^{2} \phi + \varepsilon_{z}^{s} \cos^{2} \phi & 0 & (\varepsilon_{z}^{s} - \varepsilon_{x}^{s}) \sin \phi \cos \phi \\ 0 & \varepsilon_{y}^{s} & 0 \\ (\varepsilon_{z}^{s} - \varepsilon_{x}^{s}) \sin \phi \cos \phi & 0 & \varepsilon_{x}^{s} \cos^{2} \phi + \varepsilon_{z}^{s} \sin^{2} \phi \end{pmatrix}, \tag{9}$$

for Eq. (7) as shown in Figure 2.

Making similar calculations, the energies minimized when the directors orient parallel or perpendicular to the principal axis of solid body. Namely,  $\theta = 0$  or  $\pi/2$  for Eqs. (6) and (8),  $|\phi - \theta| = 0$  or  $\pi/2$  for Eqs. (7) and (9). Finally, the EA is parallel or perpendicular to the principal axis of the dielectric permeability of the solid body, even when the principal axis of the solid body is tilted.

# IV TEMPERATURE DEPENDENCE OF THE EA FIELD ENERGY

Let us put the EA field energies as  $\pi_{\parallel}$  and  $\pi_{\perp}$  for convenience when the director is parallel and perpendicular to the principal axis of the solid body, respectively. Using the surface order parameter  $\bar{S}$ ,  $\pi_{\parallel}$  and  $\pi_{\perp}$  can be simply expressed as follows from Eqs. (4) and (5) for the free surface, and from Eqs. (6), (7), (8) and (9) for the interface.

$$\pi_{\parallel}^{\text{free}} \propto -\ln \left\{ 1 - \frac{\left(a_{\parallel} \tilde{S} - 1\right)}{\left(a_{\parallel} \tilde{S} + 1\right)} \right\},\tag{10}$$

$$\pi_{\perp}^{\text{free}} \propto -\ln \left\{ 1 - \frac{(a_{\perp}\bar{S} - 1)}{(a_{\perp}\bar{S} + 1)} \right\},\tag{10'}$$

$$\pi_{\parallel}^{\rm int} \propto -\ln \left\{ 1 - b \frac{(a_{\parallel} \bar{S} - 1)}{(a_{\parallel} \bar{S} + 1)} \right\},\tag{11}$$

$$\pi_{\perp}^{\rm int} \propto -\ln\left\{1 - b\frac{(a_{\perp}\bar{S} - 1)}{(a_{\perp}\bar{S} + 1)}\right\},$$
 (11')

where  $a_{\parallel}$  and  $a_{\perp}$  are the function of the dielectric permiability of the LC molecules, and b is also that of the solid. Here the light absorption of the LC is larger than unity,<sup>36</sup> so the approximation  $a\bar{S} \gg 1$  is valid at the temperature under consideration, and the absorption of the solid body is also large, i.e.  $b \simeq 1$ . Thus the Eqs. (10)-(11') are reduced to

$$\pi_{\parallel}^{\text{free}} \propto \ln \frac{1}{4} + \ln a_{\parallel} \, \bar{S}, \tag{12}$$

$$\pi_1^{\text{free}} \propto \ln \frac{1}{4} + \ln a_\perp \bar{S},$$
 (12')

$$\pi_{\parallel}^{\rm int} \propto \ln \frac{1}{2} + \ln a_{\parallel} \bar{S}, \tag{13}$$

$$\pi_{\perp}^{\rm int} \propto \ln \frac{1}{2} + \ln a_{\perp} \bar{S},$$
 (13')

Expanding the second terms by the power series of  $\bar{S}$  around  $\bar{S}=1$ , and considering the value of the bulk order parameter ordinarily ranges from 0.3 to 1, the terms quadratic and over in  $\bar{S}$  can be neglected. The energy of the EA field (i.e.  $\Delta\pi$ ) varies as  $\pi_{\parallel}-\pi_{\perp}$  with temperature, and the energy is finally expressed by

$$\Delta\pi \propto \Delta a \bar{S},$$
 (14)

where  $\Delta a = a_{\parallel} - a_{\perp}$ , and is constant with respect to temperature. The temperature dependence of the EA field energy is proportional to the surface order parameter. It has then been proofed that the EA field energy varies as S with temperature under the assumption of  $S = \bar{S}$  mentioned in the previous paper.<sup>1</sup>

#### V DISCUSSION AND CONCLUSION

The EA is defined by the direction of the director when the minimum energy of the van der Waals forces is realized as mentioned above. In the previous paper, we assumped that the EA behaves like as electric or magnetic field to the director in order to explain the temperature dependence of the pretilt angle. Other approaches, such as molecular dipoles or local Frederiks transition, cannot explain it as well. Introducing the concept of the EA field, the temperature dependence of the pretilt angle can be expressed well both for the free surface of the LC and the solid-LC interface.

However, there was one difficulty when the pretilt angles in the theoretical solutions degenerate to  $\pm \theta_0$ . Such a solution occurs when the EA is completely parallel or perpendicular to the surface. If the EA is slightly tilted,<sup>27</sup> one can easily show that the degenerate solutions ( $\phi \pm \theta_0$ ) resolve to unique solution  $\phi + \theta_0$  or  $\phi - \theta_0$ . Namely, there is only a single pretilted solution and its oriented direction agrees with the empirical fact that the director aligns with finite pretilt to the incident direction of the evaporation. Then the difficulty disappears.

Other interactions such as molecular dipoles, of cause, play an important role. But it is also difficult to express the temperature dependence of the pretilt angle. Probably, the effect of molecular dipole interaction with the solid may be included in the EA field.

In conclusion, the EA is parallel or perpendicular to the principal axis of the dielectric permeability of the solid, even if the principal axis is tilted. For the free surface of the LC, the EA is parallel or perpendicular to the surface. It is proven that the energy of the EA varies with the temperature and the order parameter at the surface.

Recently, we have observed the difference of order parameters between the bulk S and the surface  $\bar{S}$ .<sup>37</sup> The discrepancy between the theoretical and experimental results of the temperature dependent pretilt angles mentioned in the previous paper may be partially caused by the tilted EA and by the assumption of  $S = \bar{S}$ . Therefore, the discussion in the previous paper must be slightly revised in order to explain the surface alignment of the LC more exactly.

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