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Study on the Surface Alignment of Nematic Liquid Crystals:

Temperature Dependence of Pretilt Angles

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A simple phenomenological theory is presented for the surface or interface of nematic liquid crystals in terms of the surface order parameter Q_{ij}. The theory is based on the existence of an easy axis at the surface, so that the surface order parameter is not only a function of a director but also the easy axis.

Taking into account the concept of an easy axis field, the temperature dependence of pretilt angle can be expressed both for the free surface and the interface between liquid crystals and solid substrate. Two typical experimental results of temperature dependent angle obtained by Bouchiat and Langevin-Cruchon, and Toda, Mada and Kobayashi are compared with the theory, and good agreements are obtained qualitatively between them.

1 INTRODUCTION

Uniformly aligned thin liquid crystal (LC) films are required for applications of liquid crystal display devices (LCD) and physical investigations. It is well known that there are some techniques for obtaining the uniform alignment of LC molecules. For example, rubbing[1,2] and oblique evaporations[3] lead to completely planar samples or planar samples with small pretilt angles, and coating by an organic surfactant[4] leads to vertical alignment. The resulting initial molecular tilts at the surface (which will be referred to in this paper as the pretilt angle) were described first by Guyon, Pieranski and Boix.[5] The pretilt angle has been recognized as one of the significant parameters influencing the viewing characteristics,[6,7] response times[8] and creation or elimination of disclinations[9] in LCDs. Furthermore, physical properties, such as electro-optical properties or electrical capacitance, are sensitive to changes in the pretilt angles.[10]

In applications of these phenomena it is important to know the temperature dependence of the pretilt angle as well as its magnitude. In a previous paper, Bouchiat and Langevin-Cruchon[11] reported the tendency of the pretilt angle at the free surface of MBBA to increase with increasing temperature. A theoretical explanation has been given by Parsons[12] using the nematic-vapor interfacial tension, which is a function of the density of the LC and its ordering. In that work the interfacial tension was expressed by the form of $f\{(\mathbf{n}\cdot\nu)^2\}$, where $\mathbf{n}$ and ν are the director and the unit vector normal to the surface, respectively. On the other hand, reverse temperature dependence of the pretilt angle at the interface between glass plates and LC films was obtained by Kahn[13] in the normal twisted nematic samples and Toda, Mada and Kobayashi[14] in the planar samples. The theoretical analysis given by Parsons does not apply to the interface between a solid and an LC film.

The origin of the pretilt angle has been discussed by several authors. Meyerhofer[15] stated that it arises from the isolated asymmetric structures made by the oblique evaporation, and Goodman, McGinn, Anderson and Digeronimo[16] reported that tilted columns at the treated solid surface are the origin of the pretilt. These seem like reasonable explanations for the origin of the pretilt angle; however, the change in value of the pretilt angle with temperature (10% or more) can not be explained by only these geometrical structures. So the structural models are not complete.

In this paper a phenomenological theory of the surface of nematic LC will be described from a purely macroscopic point of view. The temperature dependence of the pretilt angle obtained by the authors mentioned above will be explained by means of a continuum theory[17-19] which has been modified to include a surface order parameter $\bar{Q}_{ij}$ and an easy axis.

2 EQUILIBRIUM THEORY

The basic principle used in this theory is Hamilton's Principle involving not only a bulk but also a surface energy which is expressed by the power series of an order parameter.

In order to express the surface energy, it is assumed that there is an easy axis[20,21] on the surface or interface, even on a free surface. The existence of the easy axis is the only respect in which the surface differs from the bulk. The concept of the easy axis was introduced first by Grandjean,[20] and ordinarily it is defined by the average direction of the long axes of the LC molecules. However, the easy axis described in this paper is treated in a different way.

The interaction between the LC and the phase in contact with it may be due mainly to the van der Waals-Lifshitz forces:[22,23] which are related to

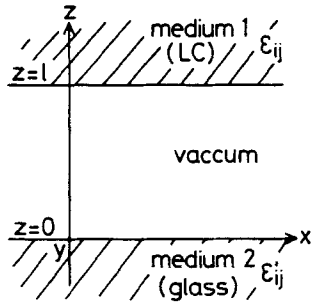

FIGURE 1 Schematic geometry considering the van der Waals–Lifshitz interaction between two phases. Each phases have a symmetric dielectric permiability ε_{ii} and ε'_{ii}.

the imaginary part of dielectric permeability at frequencies above infrared, i.e. to light absorption. In the system as shown in Figure 1, the forces F can be given by the functions of the gap l between two phases and their dielectric permeabilities ε_{ij} and ε'_{ij} as $F(l, \varepsilon_{ij}, \varepsilon'_{ij})$. Then the energy becomes $U(\varepsilon_{ij}, \varepsilon'_{ij}) = \lim_{l\to 0} \int_l^\infty F(l, \varepsilon_{ij}, \varepsilon'_{ij})dl$. The anisotropy of the light absorption of LC materials can be expressed by the refractive index. Thus the absorption of the LC becomes maximum (or minimum) when the director is parallel to the surface and minimum (or maximum) when perpendicular.[24,25] Therefore, this type of interaction energy is minimized when the directors are parallel or perpendicular to the local surface.[26] Detailed discussion about this will appear in another paper.

In this paper, the easy axis is defined by a unit vector whose direction is the same as that of the director when the minimum van der Waals–Lifshitz interaction energy is realized. Thus the easy axis must be either parallel or perpendicular to the local surface or interface, but the director of the LC molecules is not necessarily parallel to the easy axis. Namely, we will assume that the easy axis behaves like a molecular field.

The temperature dependence of some physical parameters of the LC can be expressed by a scalar order parameter S; for example, the elastic constants[18] depend approximately on S^2, and the viscosities[27] on the form of $a + bS + cS^2$. Similarly, the temperature dependence of the pretilt angle may also be expressed by the order parameter at the surface. Here, it is assumed that the molecules at the surface also rapidly rotate around their long axes and the director can be defined as in the bulk.

Therefore, the starting point from which to introduce the surface energy is the surface tensor order parameter $\bar{Q}_{ij}$. As well known, the tensor order parameter in the bulk introduced by de Gennes[28] is

$$Q_{ij} = S(n_i n_j - \tfrac{1}{3}\delta_{ij}), \tag{1}$$

where S is a scalar order parameter, and n_i and δ_{ij} are the director of the LC molecules and Kronecker's δ, respectively. The surface energy can be expressed in the form $f\{(\mathbf{n}\cdot\mathbf{d})^2\}$ where $\mathbf{d}$ is the preferred direction. Then it is necessary to make a tensor order parameter with $\mathbf{d}$ as its principal axis. Finally, the surface tensor order parameter $\bar{Q}_{ij}$ is defined as

$$\bar{Q}_{ij} = S^d(d_i d_j - \tfrac{1}{3}\delta_{ij}), \tag{2}$$

where d_i is the easy axis and S^d is the order parameter directed along the easy axis at the surface, so that S^d is a function of $\mathbf{n}$ and the temperature. This means that $\bar{Q}$ is the order parameter Q at the surface which takes its principal axis as the easy axis instead of the director. Thus $\bar{Q}$ has meaning only at the surface. In order that the part of the scalar (or microscopic) order parameters of Q and $\bar{Q}$ agree at the surface (i.e. $d_i Q_{ij} d_j = d_i \bar{Q}_{ij} d_j$), S^d must be related to S^s, which is the scalar order parameter directed along the director at the surface, by

$$S^d = \tfrac{3}{2}S^s\{(\mathbf{n}\cdot\mathbf{d})^2 - \tfrac{1}{3}\}, \tag{3}$$

as shown in Figure 2. Here, for simplicity, we assumed that the scalar order parameter is constant throughout the system, and therefore S^s can be replaced by S in Eq. (3). If $\mathbf{n}$ and $\mathbf{d}$ are parallel to each other, S^d is identical to S. This fact is clear from Eq. (3). It should be noted that S is only a function of the temperature, while on the other hand, S^d is not only a function of the temperature but also the director and the easy axis.

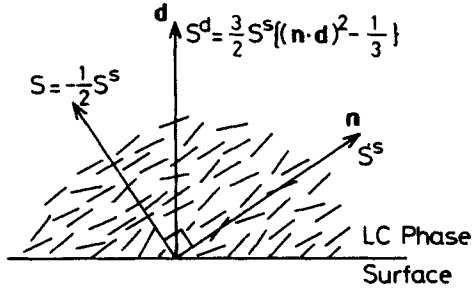

FIGURE 2 The scalar order parameter S^s and order parameter directing to the easy axis at the surface.

In addition, if the solid surface has a geometrical structure, the easy axes at each point on the surface are not constant spatially (see Figure 3(a)). But, for simplicity, attention here is restricted to the case that the easy axes are spatially constant throughout the surface under consideration, that is, the surface or interface are geometrical flat (see Figure 3(b)).

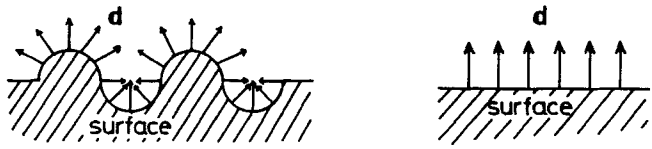

FIGURE 3 (a) The easy axes on the surface having geometrical structure. This figure shows that the easy axes are perpendicular to the local surface. The easy axes are not constant. (b) The easy axes on the flat surface.

2.1 Surface deformation energy

The deformation considered here is concerned with the easy axis, and its energy per unit area can be expanded in powers of the gradients of the surface tensor order parameter $\bar{Q}_{ij,k}$ where the order parameter varies slowly from point to point. The leading term is a constant which does not influence the deformation and can be omitted. Then, since the energy must be scalar, the next terms are quadratic in the $\bar{Q}_{ij,k}$. There are three independent combinations of the $\bar{Q}_{ij,k}$ which are quadratic in both $\bar{Q}_{ij}$ and gradient consistent with the symmetry of the nematic LC[18].

$$\bar{Q}_{ik,i}\bar{Q}_{jk,j} \tag{4-1}$$

$$\bar{Q}_{ik,j}\bar{Q}_{ik,j} \tag{4-2}$$

$$\bar{Q}_{ik,j}\bar{Q}_{jk,i} \tag{4-3}$$

Substituting Eq. (2) into expressions (4-1)–(4-3) and taking into account the fact that the easy axis is constant, terms (4-1)–(4-3) are expressed as follows.

$$\bar{Q}_{ik,i}\bar{Q}_{jk,j} = \tfrac{1}{3}d_i d_j s^d_{,i} s^d_{,j} + \tfrac{1}{9}S^d_{,i}S^d_{,i}, \tag{5-1}$$

$$\bar{Q}_{ik,j}\bar{Q}_{ik,j} = \tfrac{4}{9}S^d_{,j}S^d_{,j}, \tag{5-2}$$

$$\bar{Q}_{ik,j}\bar{Q}_{jk,i} = \tfrac{1}{3}d_i d_j S^d_{,i}S^d_{,j} + \tfrac{1}{9}S^d_{,i}S^d_{,i}, \tag{5-3}$$

where $S^d_{,i}$ is given by

$$S^d_{,i} = 3S(\mathbf{n}\cdot\mathbf{d})d_j n_{j,i}. \tag{6}$$

Thus the deformation energy at the surface can be expressed by linear combinations of Eqs. (5-1)–(5-3). Putting the coefficients of linear combinations as $\bar{L}_1$, $\bar{L}_2$ and $\bar{L}_3$, the energy is given by

$$\bar{\Lambda}_d = \tfrac{1}{2}(\mathbf{n}\cdot\mathbf{d})^2\{3S^2(\bar{L}_1 + \bar{L}_3)(d_i d_j n_{j,i})^2 + S^2(\bar{L}_1 + 4\bar{L}_2 + \bar{L}_3)(d_j n_{j,i})^2\}, \tag{7}$$

If the coefficients of Eq. (7) are put as

$$\begin{aligned} \bar{k}_1 &= 3S^2(\bar{L}_1 + \bar{L}_3), \\ \bar{k}_2 &= S^2(\bar{L}_1 + 4\bar{L}_2 + \bar{L}_3), \end{aligned} \tag{8}$$

then $\bar{k}_i$ varies as S^2 with temperature and are surface elastic constants. Finally, the surface deformation energy per unit area can be written as follows.

$$\bar{\Lambda}_d = \tfrac{1}{2}(\mathbf{n} \cdot \mathbf{d})^2\{\bar{k}_1(d_i d_j n_{j,i})^2 + \bar{k}_2(d_j n_{j,i})^2\} \tag{9}$$

If $\mathbf{n}$ at the surface is perpendicular to the easy axis, the energy $\bar{\Lambda}_d$ becomes zero, and $\bar{\Lambda}_d$ has maximum value when the director and the easy axis are parallel to each other. It is noted that $\bar{\Lambda}_d$ becomes minimum when the director is perpendicular to the easy axis, and the deformation in the bulk $n_{i,j}$ influences the energy $\bar{\Lambda}_d$. The direction of $\mathbf{d}$ is, of course, changed by the characteristics of the glass plate.

2.2 Easy axis field

At the surface, the director of a LC tends to orient with its long axis along the easy axis. The energy of orientation can be written as follows by analogy with an electric or magnetic field:[18]

$$\bar{\Lambda}_e = -\tfrac{1}{2}\pi_{ij} d_i d_j = -\tfrac{1}{2}\Delta\beta \bar{Q}_{ij} d_i d_j, \tag{10}$$

where $\Delta\beta$ is an anisotropy of alignment with respect to the easy axis. Using Eqs. (2) and (3), Eq. (10) becomes

$$\bar{\Lambda}_e = -\tfrac{1}{2}\Delta\pi\{(\mathbf{n} \cdot \mathbf{d})^2 - \tfrac{1}{3}\}, \tag{11}$$

with $\Delta\pi = S\Delta\beta$. The constant $\Delta\pi$ varies as S with temperature, like a dielectric constant,[18] and is the anisotropy of alignment constant. This means that a large magnitude of $\Delta\pi$ corresponds to strong anchoring, and if $\Delta\pi$ is equal to zero, there is no force controlling the director orientation at the surface. The energy $\bar{\Lambda}_e$ has a maximum value when the director is parallel to the easy axis. Namely, the origin of pretilt angle comes from the balance between $\bar{\Lambda}_d$ and $\bar{\Lambda}_e$.

2.3 Stable condition and torque equation

The total free energy per unit area at the surface $\bar{\Lambda}$ is

$$\bar{\Lambda} = \bar{\Lambda}_d + \bar{\Lambda}_e. \tag{12}$$

Then the total free energy throughout the system F can be given by

$$F = \int_v \Lambda(n_i, n_{i,j})dv + \int_s \bar{\Lambda}(n_i, n_{i,j})ds, \tag{13}$$

where Λ is free energy per unit volume in the bulk, and is well known as

$$\tfrac{1}{2}\{k_{11}(\text{div } \mathbf{n})^2 + k_{22}(\mathbf{n} \cdot \text{rot } \mathbf{n})^2 + k_{33}(\mathbf{n} \times \text{rot } \mathbf{n})^2\} - \tfrac{1}{2}\Delta\varepsilon(\mathbf{n} \cdot \mathbf{E})^2, \tag{14}$$

where $\Delta\varepsilon$ and $\mathbf{E}$ are the dielectric anisotropy and the electric field, respectively.

In the case of a magnetic field, the last term is replaced by $-\frac{1}{2}\Delta\chi(\mathbf{n}\cdot\mathbf{H})^2$. Minimizing F with respect to variations of n_i, the equilibrium equations are given by

$$h_i = \left(\frac{\partial\Lambda}{\partial n_{i,j}}\right)_{,j} - \frac{\partial\Lambda}{\partial n_i} = 0, \tag{15}$$

$$\bar{h}_i = \left(\frac{\partial\bar{\Lambda}}{\partial n_{i,j}}\right)_{,j} - \frac{\partial\bar{\Lambda}}{\partial n_i} - \frac{\partial\Lambda}{\partial n_{i,j}}\nu_j = 0, \tag{16}$$

where h_i is the molecular field in the bulk, $\bar{h}_i$ is the molecular field at the surface involving the easy axis field, and ν_i is a unit vector normal to the surface. The torque acting on the director by the molecular field is $\mathbf{n}\times\mathbf{h}$ without backflow in the LC layer. The torques are then obtained as

$$\Gamma = \mathbf{n}\times\mathbf{h} = 0 \quad \text{(in the bulk)}, \tag{17}$$

$$\bar{\Gamma} = \mathbf{n}\times\bar{\mathbf{h}} = 0 \quad \text{(at the surface)}. \tag{18}$$

Solving these two equations, one can get a stable conformation of an LC with arbitrary boundaries.

In order to apply the above theory to some experimental results, a more concrete formulation will be given for a non-twisted nematic LC. In this case, the director $\mathbf{n}$ can be written as follows with coordinate system shown in Figure 4. The angle θ is measured from the surface.

$$\mathbf{n} = \begin{pmatrix}\cos\theta\\ 0\\ \sin\theta\end{pmatrix} \tag{19}$$

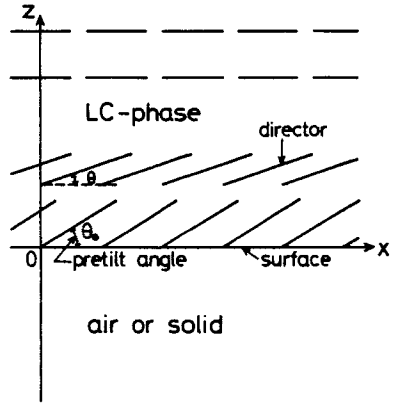

FIGURE 4 The coordinate system used in the text. The surface is in the x–y plane, and θ and θ_0 are the tilt angle and the pretilt angle, respectively, measured from the x-axis. The positive side of the z-axis is the LC phase and the negative side is an air or a solid.

From Eqs. (16) and (18), the surface torque equations are Eqs. (20) and (21) when the easy axis is perpendicular and parallel to the surface, respectively.

$$\{k_{11}\cos^2\theta + k_{33}(1+\sin^2\theta)\}\frac{d\theta}{dz} + (\bar{k}_1 - \bar{k}_2)\sin\theta\cos\theta \times \left\{(\sin^2\theta - \cos^2\theta)\left(\frac{d\theta}{dz}\right)^2 - \sin\theta\cos\theta\frac{d^2\theta}{dz^2}\right\} - \Delta\pi\sin\theta\cos\theta = 0 \quad (20)$$

$$\{k_{11}\cos^2\theta + k_{33}(1+\sin^2\theta)\}\frac{d\theta}{dz} + \bar{k}_2\sin\theta\cos\theta \times \left\{(\sin^2\theta - \cos^2\theta)\left(\frac{d\theta}{dz}\right)^2 - \sin\theta\cos\theta\frac{d^2\theta}{dz^2}\right\} + \Delta\pi\sin\theta\cos\theta = 0 \quad (21)$$

The torque equation in the bulk is given from Eqs. (15) and (17) as

$$(k_{11}\cos^2\theta + k_{33}\sin^2\theta)\frac{d^2\theta}{dz^2} - (k_{11} - k_{33})\sin\theta\cos\theta\left(\frac{d\theta}{dz}\right)^2 + \Delta\varepsilon\sin\theta\cos\theta E_z^2 = 0 \quad (22)$$

Finally, the stable condition can be obtained by these simultaneous equations: the pair of Eqs. (20) and (22), or the pair of Eqs. (21) and (22).

3 SOLUTIONS

In this section, the experimental results of temperature dependent pretilt angles obtained by several authors are expressed qualitatively as an application of the theory.

3.1 Bouchiat and Langevin-Cruchon[11]

The LC's used in their experiments were MBBA and PAA, which have a positive susceptibility anisotropy, and elastic constants satisfying the following relation.[29,30]

$$k_{11} < k_{33} \quad (23)$$

In addition, the easy axis in the case of MBBA is perpendicular at the free surface, and PAA is parallel.[26] Then the torque equations are the combination of Eqs. (20) and (22) for MBBA, and Eqs. (21) and (22) for PAA, where the last term of Eq. (22) is replaced by $\Delta\chi\sin\theta\cos\theta H_x^2$ in this case. For simplicity, it is assumed that the first term in Eq. (20) is very small compared with the second or third terms. The torque equations for MBBA are given by the following equations.

$$\bar{k} \sin\theta \cos\theta \left\{(\sin^2\theta - \cos^2\theta)\left(\frac{d\theta}{dz}\right)^2 - \sin\theta\cos\theta\frac{d^2\theta}{dz^2}\right\} - \frac{\Delta\pi}{k_{11}}\sin\theta\cos\theta = 0, \quad (24)$$

$$(1 - k\sin^2\theta)\frac{d^2\theta}{dz^2} - k\sin\theta\cos\theta\left(\frac{d\theta}{dz}\right)^2 + \frac{\Delta\chi}{k_{11}}\sin\theta\cos\theta H_x^2 = 0, \quad (25)$$

where $\bar{k}$ and k are $(\bar{k}_1 + \bar{k}_2)/k_{11}$ and $(k_{11} - k_{33})/k_{11}$, respectively, and are constant with temperature.

The particular solutions are obtained from

$$\sin\theta\cos\theta = 0, \quad (26)$$

giving $\theta = 0$ or $\theta = \pi/2$. These solutions correspond to completely homogeneous and homeotropic alignment, respectively, and have no temperature dependence under any condition.

Putting $\sin^2\theta = x$ and $\Delta\chi\bar{k}H_x^2/\Delta\pi = C_0^2$, the general solution of the simultaneous Eqs. (24) and (25) is

$$\frac{\Delta\pi}{k_{11}} = \frac{\bar{k}c^2\{-kx^2 + 2x - 1\}}{(1 - kx)^2 + C_0^2(-3x^2 + 2x)}, \quad (27)$$

where c^2 is an integral constant. The left-hand side of Eq. (27) varies as 1/S with temperature. In the experiment, the applied magnetic field was weak (below the threshold). In this case the approximation of $k \gg C_0^2$ is valid, and Eq. (27) can be simplified to

$$\frac{\Delta\pi}{k_{11}} = \frac{\bar{k}c^2\{-kx^2 + 2x - 1\}}{(1 - kx)^2}. \quad (28)$$

The curve of this equation with respect to x is shown in Figure 5, and must be

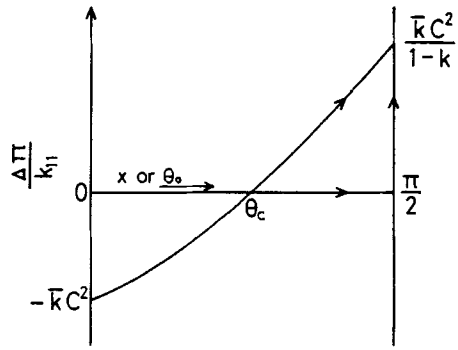

FIGURE 5 Curve of eq. (28) with respect to x (or θ_0), θ_c is $\{(1 - k)^{-1/2} - 1\}/k$. Arrows show a tendency of increasing temperature.

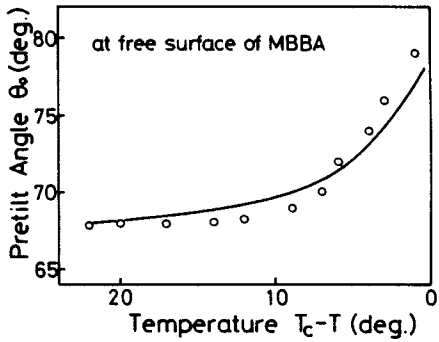

FIGURE 6 Temperature dependence of pretilt angle for the free surface of MBBA. Plotted points are experimental results obtained by Bouchiat *et al.*, and the solid line shows the theoretical result selecting $\alpha = 0.23$ in Eq. (28').

positive. The zero point θ_c is about 47° in the case of MBBA ($k = -0.4$).[30] A change in sign which occurs at θ_c will be discussed in the next section. The comparison between their experimental result and the theoretical one is shown in Figure 6; Eq. (28) was modified to

$$\frac{\alpha}{S} = \frac{-3x^2 + 2x - 1}{(1 - kx)^2}, \tag{28'}$$

and the value $\alpha = 0.23$ was selected by a least squares method. The order parameter S used in this computation was the data of Jen *et al.*[31] The validity of the value of α will also be discussed in the next section.

3.2 Toda, Mada, and Kobayashi[14]

The LC is a 4:1 by weight mixture of 5CB and 6OCB, having a positive dielectric anisotropy, and $k_{11} > k_{33}$. The easy axis is parallel to the glass plate. The torque equations are as follows neglecting the first term of Eq. (21).

$$\bar{k}' \sin\theta\cos\theta\left\{(\sin^2\theta - \cos^2\theta)\left(\frac{d\theta}{dz}\right)^2 - \sin\theta\cos\theta\frac{d^2\theta}{dz^2}\right\} + \frac{\Delta\pi}{k_{11}}\sin\theta\cos\theta = 0, \tag{29}$$

$$(1 - k\sin^2\theta)\left(\frac{d\theta}{dz}\right)^2 + \frac{\Delta\varepsilon}{k_{11}}\sin^2\theta E_z^2 = c^2, \tag{30}$$

where c^2 is an integral constant, and $\bar{k}'$ is k_2/k_{11}. The coefficient $\bar{k}'$ is constant with temperature.

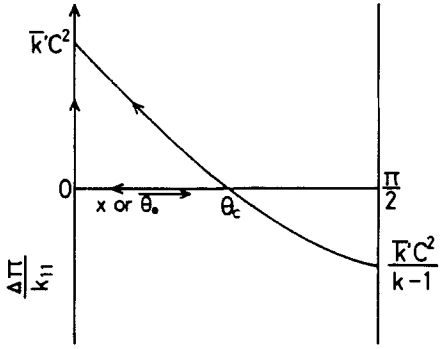

FIGURE 7 Curve of eq. (31) with respect to x (or θ_0). θ_c is $\{1 - (1 - k)^{-1/2}\}/k$. Arrows show a tendency of increasing temperature.

Similarly, the particular solution is $\theta = 0$ or $\theta = \pi/2$. This agrees with the experimental results obtained by Toda *et al.* Furthermore, this solution also agrees with the case of PAA investigated by Bouchiat and Langevin–Cruchon.

The general solution is given by the following equation putting $\sin^2\theta = x$, $\Delta\varepsilon\bar{k}'E_z^2/\Delta\pi = C_0^2$.

$$\frac{\Delta\pi}{k_{11}} = \frac{\bar{k}'c^2(kx^2 - 2x + 1)}{(1 - kx)^2} \tag{31}$$

The pretilt angles were measured by the magneto-capacitive null method, and the applied electric field for measuring capacitance was very small. Therefore

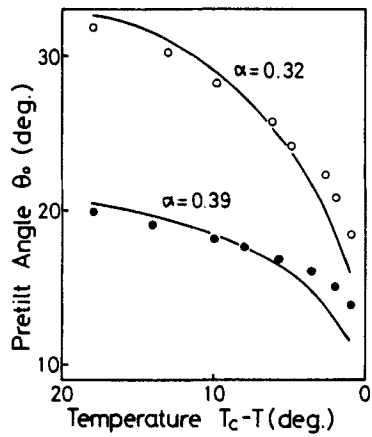

FIGURE 8 Temperature dependence of pretilt angle for the interface between glass plate and the LC. Plotted points are two experimental results obtained by Toda *et al.*, and solid lines are theoretical results where $\alpha = 0.32$ and 0.39 in Eq. (31').

an approximation of $k \gg C_0^2$ is also used here. The curve of Eq. (31) with respect to x is shown in Figure 7, and must be positive. The θ_c is about 54° in this case ($k = 0.4$). The comparison is shown in Figure 8; Eq. (31) was modified to

$$\frac{\alpha}{S} = \frac{kx^2 - 2x + 1}{(1 - kx)^2}, \tag{31'}$$

and the values $\alpha = 0.32$ and 0.39 were selected by a least squares method.

4 DISCUSSION

The temperature dependences of pretilt angles are explained using torque equations. The origin of the pretilted alignment is the balance between $\bar{\Lambda}_d$ and $\bar{\Lambda}_e$, which correspond to the bulk deformation energy and (electric or magnetic) field energy, respectively.

The most interesting problem appears in Eqs. (28) and (31) (see also Figure 5 and 7), i.e. the negative value of $\Delta\pi/k_{11}$ occurs below (or above) θ_c. This fact can be interpreted physically as follows. In the experiment of Toda *et al.*, an alignment having a pretilt angle greater than 54° never arises using such LC material and SiO evaporation in their experiment. It is well known that higher pretilted alignment (45°–60°) is difficult to make uniformly by oblique evaporation.[15,32] This is explained by the negative values of Eq. (31), from which the maximum pretilt angle θ_c can be calculated.

Next, we estimate the value of α in Eq. (31'). From Eqs. (31) and (31'), α is equal to $\Delta\pi/\bar{k}_2 c^2$. Here, the order of c^2 is $(d\theta/dz)^2$ from Eq. (30), and further, the order of $\Delta\pi/\bar{k}_2$ is also $(d\theta/dz)^2$ from Eq. (29). Then the order of α is unity. This fact is again understood more easily from the right-hand side of Eqs. (28') and (31'). The values of α calculated in the last section are valid.

The descrepancy between experimental and theoretical results, especially near the clearing point, may result from approximations such as the omission of the first term in Eq. (20) and the assumption that the order parameter in the bulk and the order parameter at the surface are equal.

5 CONCLUSION

We have demonstrated that the temperature dependence of the pretilt angle obtained by several authors can be explained by introducing the concept of the easy axis field and considering the surface energy. Completely homogeneous and homeotropic samples do not have temperature dependent tilt angles, and are deformation free in the bulk. The pretilted samples are slightly deformed in the bulk (near the surface), because the balance between $\bar{\Lambda}_d$ and

$\bar{\Lambda}_e$ is needed for pretilted alignment at the surface (as can be shown from Eq. (9)). These samples, more or less, have the temperature dependence of pretilt angles.

Good agreement between experimental and theoretical results are obtained, so that the theory is an effective tool for phenomenological analysis of surface properties. Furthermore, if the coefficients are determined, more quantitative explanation will be possible. Unfortunately, it is not yet established how to determine the coefficients $\bar{k}_i$ and $\Delta\pi$. It will be necessary to develop a method to measure these values.

In this paper, we have restricted our attention to the constant easy axis and its uniaxial field. However, when the substrate is treated by oblique evaporation, the easy axis is no longer constant and its field may be biaxial. When **d** is not constant and the LC is twisted, the stable condition is given by 6 torque equations. It is difficult to solve these equations analytically, and further calculation will be necessary to understand the more detailed characteristics of the surface or interface.

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