Experimental determination of the effective splay-bend elastic constant

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The temperature-induced surface alignment transitions in nematic liquid crystals are analyzed. It is shown that it is possible to interpret the experimental data by means of an elastic model in which the effective splay-bend surfacelike elastic constant is taken into account. This effective elastic constant is defined as the sum of the usual splay-bend and spontaneous splay elastic constant. In this framework the experimental data seem to indicate that the easy axis characterizing the nematic-substrate interaction is independent of the liquid crystal. It depends only on the evaporation geometry (we use flat glass plates vacuum coated by SiO) and on the surfactant dissolved in the liquid crystal. The value of the effective splay-bend elastic constant is obtained for three different liquid crystals in the nematic phase.

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I. INTRODUCTION

The surface properties of a nematic liquid crystal limited by a solid substrate are usually described in terms of a surface anchoring energy g. There exist a lot of papers devoted to the origin of g [1]. g is expected to be a function of the physical properties of the substrate and of the liquid crystal [2]. The surface nematic liquid crystal orientation minimizing g is usually called the easy direction [3]. The actual surface nematic liquid crystal orientation, in a sample presenting an elastic deformation, may coincide or not with the easy direction. The difference between the actual orientation of the nematic liquid crystal and its easy direction, for a given bulk deformation, gives an idea about the anchoring strength [4]. The surface orientation may or may not depend on the temperature.

Recent experimental investigations show that the temperature may be responsible for a kind of surface instability, called the temperature surface transition [5–10]. Several papers are devoted to the analysis of the temperature dependence of the nematic liquid crystal orientation [11–15]. In a recent paper one of us has proposed an elastic model to interpret the temperature surface transitions [16].

In this paper we want to extend the analysis presented in [16], and to compare the theoretical predictions of this model with the experimental data relevant to the temperature surface transitions obtained in our laboratory for different liquid crystals. We will show that the easy axis imposed by an obliquely evaporated surface [8] to a nematic liquid crystal doped with a surfactant for homeotropic alignment is independent of the liquid crystal. The macroscopic, and experimentally detectable, orientation of the nematic liquid crystal can be interpreted in terms of the effective splay-bend elastic constant. We will show, furthermore, that, by taking into account the different temperature behaviors of the effective splay-bend and the usual elastic constants, it is possible to interpret the observed temperature variation of the average orientation. The best fit gives us also an experimental determination of the effective splay-bend surfacelike elastic constant.

Our paper is organized as follows. In Sec. II the model is presented, and some special predictions are discussed. The different contributions to the effective splay-bend elastic constant are discussed in Sec. III. The experimental part is described in Sec. IV. Section V is devoted to discussion of the experimental results and to the conclusions.

II. THEORETICAL MODEL

Let us consider a nematic liquid crystal sample, which will be supposed, for simplicity, semi-finite. The Cartesian frame used in our analysis has the $(x$-$y)$ plane coinciding with the surface limiting the nematic liquid crystal, occupying the $z > 0$ half space. The problem will be supposed one dimensional, i.e., all the physical quantities depend only on the z coordinate. Furthermore, the nematic director **n** is supposed to be everywhere parallel to the $(x$-$z)$ plane. The angle made by **n** with the z axis, the tilt angle, will be indicated by $\phi = \phi(z)$. In this framework the total elastic energy per unit surface is given by

$$F = \int_0^\infty f(\phi, \phi', \phi'') dz + g(\phi_0, \phi_0') , \qquad (1)$$

where the bulk elastic constant energy density $f(\phi, \phi', \phi'')$ is

$$f(\phi, \phi', \phi'') = \tfrac{1}{2} k \phi'^2 + \tfrac{1}{2} k^* \phi''^2 , \qquad (2)$$

and the surface elastic energy $g(\phi_0, \phi_0')$ is

$$g(\phi_0, \phi_0') = \tfrac{1}{2} w \sin^2(\phi_0 - \phi_e) + \tfrac{1}{2} \bar{K}_{13} \sin(2\phi_0) \phi_0' . \qquad (3)$$

In these equations the prime means a derivative with

respect to z, and $\phi_0 = \phi(0)$, $\phi_0' = \phi'(0)$. Expression (2) for $f(\phi, \phi', \phi'')$ generalizes the well known elastic energy density proposed long ago by Frank [17] in the limit of small deformations. k is the usual elastic constant, and k^* the second-order elastic constant [18,19]. In (3) the first term on the right-hand side is the Rapini-Papoular expression [3] for the surface anchoring energy, having anchoring strength w and easy direction ϕ_e. The second term is connected with the surfacelike elastic constant k_{13} introduced by Nehring and Saupe [20] and with the surface energy proposed by Dubois-Violette and Parodi [21]. The origin of these two contributions to the total surface energy will be discussed in the next section. The minimization of (1) gives [22]

$$\frac{\partial f}{\partial \phi} - \frac{d}{dz}\frac{\partial f}{\partial \phi'} + \frac{d^2}{dz^2}\frac{\partial f}{\partial \phi''} = 0 \ , \quad z \in [0, \infty] \ , \qquad (4)$$

for the bulk, with the boundary conditions

$$-\left[\frac{\partial f}{\partial \phi'} - \frac{d}{dz}\frac{\partial f}{\partial \phi''}\right] + \frac{\partial g}{\partial \phi} = 0 \ , \quad z = 0 \ , \qquad (5a)$$

$$-\frac{\partial f}{\partial \phi''} + \frac{\partial g}{\partial \phi'} = 0 \ , \quad z = 0 \ , \qquad (5b)$$

and

$$\lim_{z \to \infty}\left[\frac{\partial f}{\partial \phi'} - \frac{d}{dz}\frac{\partial f}{\partial \phi''}\right] = 0 \ , \qquad (6a)$$

$$\lim_{z \to \infty}\left[\frac{\partial f}{\partial \phi''}\right] = 0 \ . \qquad (6b)$$

By observing that f is independent of ϕ, the quantity

$$\mu = -\frac{\partial f}{\partial \phi'} + \frac{d}{dz}\frac{\partial f}{\partial \phi''} \qquad (7)$$

is a constant. Using (7), the boundary conditions (5a) and (6a) may be rewritten as

$$-\mu + \frac{\partial g}{\partial \phi} = 0 \ \text{ for } z = 0 \ , \qquad (5c)$$

and

$$\mu \to 0 \ \text{ for } z \to \infty \ . \qquad (6c)$$

Consequently the function $\phi(z)$ we are looking for is the solution of the differential equation

$$-\frac{\partial f}{\partial \phi'} + \frac{d}{dz}\frac{\partial f}{\partial \phi''} = 0 \ , \qquad (8)$$

satisfying the boundary conditions (5b),(5c) and (6b),(6c).

By using (2) and (3), Eq. (8) and the relevant boundary conditions become

$$\phi' - b^2\phi''' = 0 \ , \qquad (9)$$

and

$$\frac{w}{2}\sin[2(\phi_0 - \phi_e)] + \bar{k}_{13}\cos(2\phi_0)\phi_0' = 0 \ , \qquad (10a)$$

$$-k^*\phi_0'' + \tfrac{1}{2}\bar{k}_{13}\sin(2\phi_0) = 0 \ , \qquad (10b)$$

at $z = 0$, and

$$\phi'' \to 0 \ \text{ for } z \to \infty \ . \qquad (11)$$

In (9) $b^2 = (k^*/k)$ is a mesoscopic length [18].

From Eq. (9) one deduces that the quantity

$$p = \phi - b^2\phi'' \qquad (12)$$

is z independent. Consequently, by using (11), $\phi(z)$ is a solution of the bulk equation

$$\phi - b^2\phi''(z) = \phi_b \qquad (13)$$

where $\phi_b = \lim_{z \to \infty}\phi(z)$. The solution of (13) is

$$\phi(z) = \phi_b + (\phi_0 - \phi_b)\exp(-z/b) \ , \qquad (14)$$

where ϕ_b and ϕ_0 are determined by the boundary conditions (10a) and (10b). By substituting (14) into (10a) and (10b), simple calculations give

$$\frac{1}{2L}\sin[2(\phi_0 - \phi_e)] - \frac{\bar{k}_{13}}{k}\frac{\phi_0 - \phi_e}{b}\cos(2\phi_0) = 0 \ , \qquad (15)$$

and

$$\phi_0 - \phi_b = \frac{1}{2}\frac{\bar{k}_{13}}{k}\sin(2\phi_0) \ , \qquad (16)$$

where $L = (k/w)$ is the extrapolation length [3]. By substituting (16) into (15) we derive, finally, that ϕ_0 is given by

$$\frac{\sin[2(\phi_0 - \phi_e)]}{\sin(4\phi_0)} = \frac{L}{2b}\left[\frac{\bar{k}_{13}}{k}\right]^2 \ . \qquad (17)$$

ϕ_0 is the actual value of the surface tilt angle. When this value has been determined, from Eq. (16) one obtains

$$\phi_b = \phi_0 - \frac{1}{2}\frac{\bar{k}_{13}}{k}\sin(2\phi_0) \qquad (18)$$

for the bulk value of the nematic tilt angle. In the case in which $L \ll b$, i.e., the anchoring energy is infinite, (17) gives $\phi_0 = \phi_e$, as expected.

It is important to stress that the quantity experimentally detectable is ϕ_b, because $\phi(z) - \phi_b$ is different from zero only in the surface layer whose thickness is of the order of b, which is negligible with respect to the thickness of the usual samples. In fact, the optical methods, or the method called "null magnetic field," measure the quantity

$$\langle \sin^2\phi \rangle_d = \frac{1}{d}\int_0^d \sin^2\phi(z)dz$$

$$= 2\frac{b}{d}\langle \sin^2\phi \rangle_b + \frac{d - 2b}{d}\sin^2\phi_b \ , \qquad (19)$$

where

$$\langle \sin^2\phi \rangle_b = \frac{1}{b}\int_0^b \sin^2\phi(z)dz = \frac{1}{b}\int_{d-b}^d \sin^2\phi(z)dz \ . \qquad (20)$$

Since $b/d \ll 1$, (19) shows that $\langle \sin^2\phi \rangle \approx \sin^2\phi_b$, as stated before.

In the following we assume that the anchoring energy is characterized by an infinite anchoring strength w, and

hence that $\phi_0 = \phi_e$ and ϕ_b is given by

$$\phi_b = \phi_e - \frac{1}{2}\frac{\bar{k}_{13}}{k}\sin(2\phi_e) . \tag{21}$$

In this framework the temperature dependence of ϕ_b is due to the different temperature behaviors of $\bar{k}_{13}$ and k.

As discussed elsewhere, k_{13} and k depend on the temperature according to the laws [23,24]

$$\bar{k}_{13} = c_1 S + c_2 S^2 , \tag{22}$$

and [25]

$$k = k_2 S^2 , \tag{23}$$

where c_1, c_2, and k_2 are temperature independent. The scalar order parameter S is given by [25]

$$S(T) = \Delta \left[1 - \frac{T}{T_c}\right]^{1/2} , \tag{24}$$

where Δ is a constant and T_c a temperature a little bit higher than the nematic $(N) \rightarrow$ isotropic (I) phase transition temperature. By substituting (22), (23), and (24) into (21) we obtain

$$\phi_b(T) = \phi_e - \frac{1}{2}\left[\frac{A}{\sqrt{T_c - T}}\right]\sin(2\phi_e) , \tag{25}$$

where the parameters A and B are defined by

$$A = \frac{\sqrt{T_c}}{\Delta}\frac{c_1}{k_2} \quad \text{and} \quad B = \frac{c_2}{k_2} . \tag{26}$$

Equation (25) gives the temperature dependence of ϕ_b, the quantity experimentally detectable.

III. THE EFFECTIVE SPLAY-BEND ELASTIC CONSTANT

In our theoretical model the surface energy is supposed of the kind (3). In this framework, the phenomenological description of the nematic liquid crystal is given in terms of the elastic constants k, k^*, $\bar{k}_{13}$, and w. In particular, for what concerns the nematic liquid crystal–substrate interface, the anisotropic part of the surface tension is supposed to be [3]

$$g(\phi_0) = \tfrac{1}{2}w \sin^2(\phi_0 - \phi_e) . \tag{27}$$

The other term appearing in (3) is obtained by adding two different contributions. One, which is a bulk term of the kind $k_{13}\text{div}(\mathbf{n}\,\text{div}\mathbf{n})$, is obtained by interaction over the volume of the nematic sample [20]. The other one is a surface term of the kind

$$g_{\text{DVP}}(\phi_0,\phi_0') = \tfrac{1}{2}k_{\text{DVP}}\sin(2\phi_0)\phi_0' , \tag{28}$$

proposed for the first time by Dubois-Violette and Parodi [21] long ago. The term g_{DVP}, has the same form as the k_{13} contribution. In fact, following the Gauss theorem, is

$$\int\int\int_\tau k_{13}\text{div}(\mathbf{n}\,\text{div}\mathbf{n})d\tau = \oiint_\Sigma k_{13}\mathbf{v}\cdot\mathbf{n}\,\text{div}\mathbf{n}\,d\tau ,$$

where τ is the volume of the nematic sample limited by

the closed surface Σ and $\mathbf{v}$ is the outward normal. In our case, in which the sample is supposed semi-infinite, the contribution to the surface energy for unit surface is found to be

$$g_{13} = \tfrac{1}{2}k_{13}\sin(2\phi_0)\phi_0' .$$

It follows that the effective splay-bend elastic constant introduced in (3) is given by

$$\bar{k}_{13} = k_{\text{DVP}} + k_{13} .$$

Consequently, the experimental data relevant to $\phi_b(T)$ give information on $\bar{k}_{13}$ instead of the k_{13} elastic constant alone [see Eq. (21)]. However, it is important to stress that k_{13} never enters in the elastic theory alone. Only $\bar{k}_{13}$ appears, which is the only physical parameter detectable and important in the elastic theory for nematic liquid crystals.

Now we want to show that k_{DVP} is connected with a bulk contribution to the elastic energy, called spontaneous splay. Furthermore, we will show that k_{13} and k_{DVP} originate from the same intermolecular interaction. In order to show this, let us recall the pseudomolecular approach to evaluating the nematic liquid crystal elastic constants. The starting assumption is a two body interaction law of the kind $G(\mathbf{n},\mathbf{n}',\mathbf{r})$ between two small volumes $d\tau$ and $d\tau'$ located in $\mathbf{R}$ and in $\mathbf{R}'=\mathbf{R}+\mathbf{r}$, characterized by the average nematic orientation $\mathbf{n}=\mathbf{n}(\mathbf{R})$ and $\mathbf{n}'=\mathbf{n}(\mathbf{R}')$, respectively [26]. In general, $G(\mathbf{n},\mathbf{n}',\mathbf{r})$ may be expanded in power series in the following manner:

$$G(\mathbf{n},\mathbf{n}',\mathbf{r}) = -\sum_{abc} J_{a,b,c}(r)(\mathbf{n}\cdot\mathbf{u})^a(\mathbf{n}'\cdot\mathbf{u})^b(\mathbf{n}\cdot\mathbf{n}')^c , \tag{29}$$

where $\mathbf{u}=\mathbf{r}/r$ and the coupling constants $J_{a,b,c}$ depend only on the modulus of $\mathbf{r}$ and not on its direction, since the described interaction G must be invariant with respect to rotation. In the framework $|\mathbf{n}'-\mathbf{n}| = |\mathbf{n}(\mathbf{R}')-\mathbf{n}(\mathbf{R})| \ll 1$, it is possible to expand (29) in power series of $\delta\mathbf{n}=\mathbf{n}'-\mathbf{n}$. After that it is possible to expand δn_i in power series of the components of $\mathbf{r}$. All these calculations are standard and described in great detail in [26]. The results is that, in the mean field approximation, the elastic energy density of a nematic liquid crystal is given by

$$f = f_0 + \tfrac{1}{2}[k_{11}(\text{div}\mathbf{n})^2 + k_{22}(\mathbf{n}\cdot\text{rot}\mathbf{n})^2$$
$$+ k_{33}(\mathbf{n}\times\text{rot}\mathbf{n})^2] + k_{13}\text{div}(\mathbf{n}\,\text{div}\mathbf{n})$$
$$+ (k_{22}+k_{24})\text{div}(\mathbf{n}\,\text{div}\mathbf{n}+\mathbf{n}\times\text{rot}\mathbf{n}) + k_1\text{div}\mathbf{n} . \tag{30}$$

In (30) f_0 is the energy of the undeformed state, and k_{11}, k_{22}, k_{33}, k_{13}, and k_{24} the usual elastic constants of nematic liquid crystals [20]. Finally, k_1 is constant linear in the first-order spatial derivatives of $\mathbf{n}$ called spontaneous splay [26]. In the spherical approximation for the interaction volume [27] the usual elastic constants are found to be

$$k_{11} = \frac{1}{2} \sum_{abc} \frac{J_4(a,b,c)}{(a+b+1)(a+b+3)} \left[\frac{3ab}{a+b-1} + c \right] ,$$

$$k_{22} = \frac{1}{2} \sum_{abc} \frac{J_4(a,b,c)}{(a+b+1)(a+b+3)} \left[\frac{ab}{a+b-1} + c \right] ,$$

$$k_{33} = \frac{1}{2} \sum_{abc} \frac{J_4(a,b,c)}{(a+b+3)} \left[\frac{ab}{a+b+1} + c \right] ,$$

$$k_{13} = -\frac{1}{2} \sum_{abc} J_4(a,b,c) \frac{b}{(a+b+1)(a+b+3)} ,$$

$$k_{22} + k_{24} = \frac{1}{4} \sum_{abc} J_4(a,b,c) \frac{3b+c}{(a+b+1)(a+b+3)} . \tag{31}$$

where

$$J_4(a,b,c) = 4\pi \int_{r_0}^{\infty} J_{a,b,c}(r) r^4 dr . \tag{32}$$

In (32) r_0 is of the order of the molecular dimension [28]. The elastic constant of spontaneous splay is given by [26]

$$k_1 = -\frac{1}{4} \sum_{abc} \int \int \int_{V_N} J_{a,b,c}(r) b [(\mathbf{n} \cdot \mathbf{u})^{a+b-1}$$

$$- (\mathbf{n} \cdot \mathbf{u})^{a+b+1}]$$

$$\times r^3 dr \, d\Omega , \tag{33}$$

where V_N is the interaction volume. In the bulk, where V_N is a complete sphere, k_1 is identically zero because in the expansion (29) the $\mathbf{n} \equiv -\mathbf{n}$ equivalence implies that $a+b$, $b+c$, and $a+c$ are even numbers. In a surface layer, whose thickness is a few molecular dimensions, V_N is not a complete sphere and k_1 is not identically zero. Furthermore, it is odd in $\mathbf{n}$ as follows from (33), as expected. It reaches its maximum value on the surface limiting the sample.

By comparing (33) with the expression for k_{13} given in (31), we can derive that k_1 has to be taken into account whenever k_{13} plays some role. Furthermore, by taking into account that $k_1(\mathbf{n}) = -k_1(-\mathbf{n})$, as follows from (33), we have that the energy term connected to k_1, which is $k_1 \text{divn}$, may be rewritten as

$$k_1 \text{divn} = \frac{1}{2} k_{DVP} \mathbf{n} \cdot \mathbf{v} \, \text{divn} , \tag{34}$$

where now $k_{DVP}(\mathbf{n}) = k_{DVP}(-\mathbf{n})$. Hence the Dubois-Violette–Parodi term is connected with the spontaneous splay. It is equivalent to a surface term because k_1, as underlined before, is different from zero only in a surface layer whose thickness is a few molecular dimensions.

From the above it follows that in all the experimental analyses it is possible to derive information only on the effective splay-bend elastic constant $\bar{k}_{13} = k_{13} + k_{DVP}$. Very recently Pergamenshchik [30] has shown, in a phenomenological manner, that the term (28) is all the time negligible with respect to the k_{13} term. According to our pseudomolecular analysis, this is not usually true.
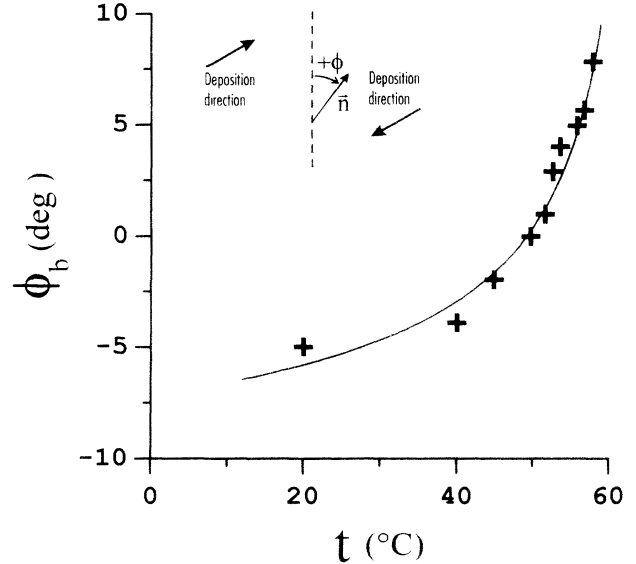

FIG. 1. Average nematic liquid crystal orientation vs the temperature for the NP8A liquid crystal. The tilt angle is measured with respect to the geometrical normal of the substrate. The sample assembly and the definition for the sign of the tilt angle are given in the inset.

IV. EXPERIMENT

We have measured the average tilt angle in nematic liquid crystal samples of thickness $d \sim 30 \mu m$. The liquid crystals used in our experiments are ZLI 1623 ($T_{N-I} = 80\,°C$), ZLI 997 ($T_{N-I} = 78\,°C$), and NP8A ($T_{N-I} = 60\,°C$) by Merck, containing the surfactant ZLI 584, giving homeotropic orientation on a flat surface, dissolved inside. T_{N-I} is the nematic→isotropic phase transition temperature. The samples were prepared from plane glass surfaces on which a SiO layer was obliquely deposited by vacuum evaporation at an incident angle of
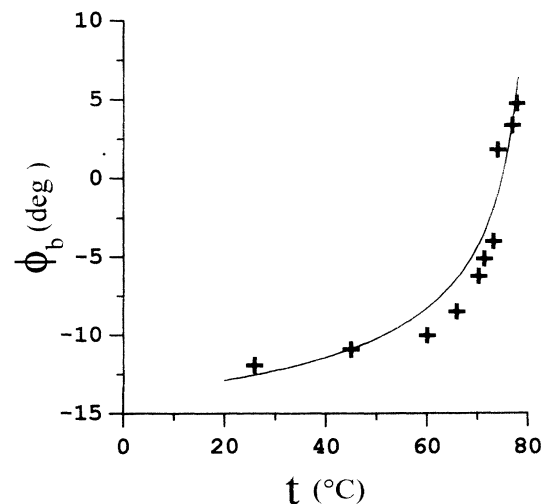

FIG. 2. As in Fig. 1 for the ZLI 997 liquid crystal.

60° (with respect to the geometrical normal). Usually this kind of surface gives, for a pure nematic liquid crystal, a planar anchoring with the easy axis perpendicular to the evaporation direction [14]. The two glasses forming a cell were mounted so that symmetrical boundary conditions were obtained (see Fig. 1). The observed average orientation in the sample, because of the presence of the surfactant, was tilted at an angle ϕ with respect to the surface normal. The other aspects of technique (the sample realization, control of temperature, and optical determination of the average orientation of the nematic liquid crystals) are described in detail in Ref. [8]. In the present investigation the average orientation has also been measured using the null magnetic field method. The experimental data have been obtained with three different sets of samples. The results are shown in Figs. 1–3.

We have fitted the experimental data by means of Eq. (25) obtained by supposing infinite anchoring energy, and hence ϕ_e is supposed to be temperature independent. The parameters of the best fit are reported in Table I. We stress that T_c is a little bit larger than T_{N-I}, as expected. From the value of T_c obtained by the best fit and taking into account that at room temperature the scalar order parameter is of the order of 0.6, we have obtained the coefficient Δ appearing in (24). The value of ϕ_e has been found to be approximately the same for the three sets of experimental data.

V. DISCUSSION

The parameters of the best fit reported in Table I give us the opportunity to derive important conclusions about the nematic liquid crystal–surface interaction. In fact, from the experimental result that ϕ_e is approximately the same for different liquid crystals containing a surfactant and limited by the same surface, we may deduce that

(i) The easy axis characterizing the nematic liquid crystal–substrate interaction depends on the angle of evaporation and on the surfactant, but it is independent of the liquid crystal;

(ii) the anchoring strength is very large, and the anchoring may be supposed strong;

(iii) the observable nematic tilt angle ϕ_b is different from the true surface tilt angle ϕ_0; it depends on the elastic properties of the nematic liquid crystal by means of the elastic ratio $\bar{k}_{13}/k$.

A possible consequence of the above reported interpretation of the experimental data is that usually the nematic liquid crystal–substrate interaction is characterized by strong anchoring energy. The experimentally detectable anchoring energy strength originates from the elastic properties of the liquid crystal. The temperature depen-
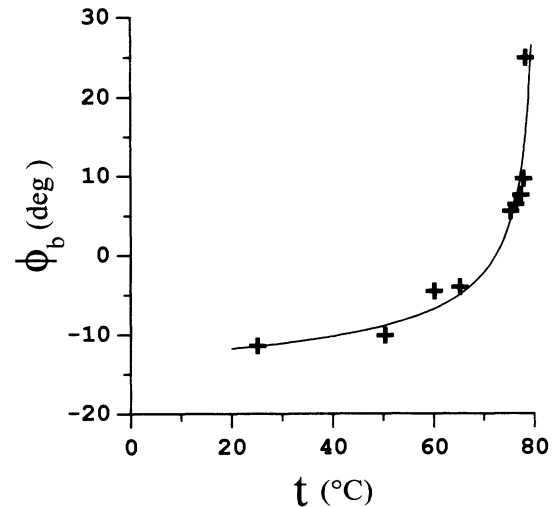

FIG. 3. As in Fig. 1 for the ZLI 1623 liquid crystal.

dence of the average tilt angle may be deduced by supposing that the surface scalar order parameter is equal to the bulk one.

Let us consider now the last three columns of Table I. They represent an experimental determination of the effective splay-bend surfacelike elastic constant. In our paper, as has been stressed before, this effective elastic constant is defined as the sum of the usual splay-bend elastic constant k_{13} introduced by Nehring and Saupe [20] and the spontaneous splay elastic constant k_1 introduced by Dubois-Violette Parodi [21]. Up to now only one other estimation of this parameter has been published [31], but since the theoretical analysis of the experimental data was based on a wrong theory [32], just its order of magnitude is meaningful. Our analysis shows that the linear component c_1 in the scalar order parameter of the $\bar{k}_{13}$ elastic constant is smaller than the quadratic component c_2 in the same parameter. The analysis shows, furthermore, that c_2 is of the same order of magnitude as the usual Frank's elastic constant k_2. c_1 is found to be negative, whereas c_2 is positive. The trend of $\bar{k}_{13}/k$ vs the temperature, evaluated with the parameters of the best fits, for the liquid crystals considered is shown in Fig. 4. At room temperature (20 °C) the ratio $\bar{k}_{13}/k$ is of the order of 1.51 (NP8A), 1.79 (ZLI 997), and 1.75 (ZLI 1623), i.e., positive and close to 2. The only one theoretical estimation of this ratio has been done for the induced-dipole–induced-dipole interaction [28,29]. According to the theoretical model of Refs. [28,29], for nearly homeotropic nematic samples $\bar{k}_{13}/k$ is of the or-

TABLE I. Best-fit values of parameters obtained for various liquid crystals.

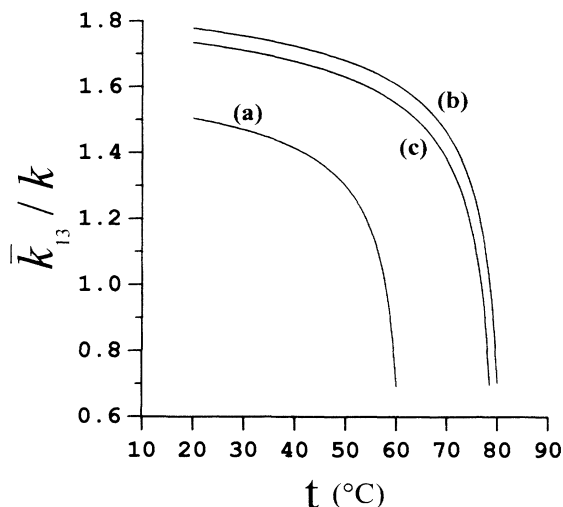| Liquid crystal	(c_1/c_2)	(c_1/k_2)	(c_2/k_2)	$(\bar{k}_{13}/k)$	ϕ_e (deg)	t_c(°C)	t_{N-I} (°C)
NP8A	−0.08	−0.1	1.7	1.51	35	62.2	60
ZLI 997	−0.10	−0.2	2.0	1.78	35	82.3	78
ZLI 1623	−0.10	−0.2	2.0	1.74	35	81.0	80

FIG. 4. Ratio k_{13}/k vs the temperature evaluated by means of the parameters of the best fit. (a) NP8A, (b) ZLI 997, and (c) ZLI 1623.

der of -1.2 (see the Appendix). By comparing the theoretical prediction (deduced on the hypothesis that the dispersion forces are the only ones responsible for the nematic phase) and the experimental values it is possible

to conclude that the dispersion forces are not the most important ones for the nematic phase considered by us. This is not surprising, because other forces, like steric ones, are expected to be more important in organic molecules giving rise to nematic phases.

ACKNOWLEDGMENTS

APPENDIX

In this Appendix we want to evaluate the $\bar{k}_{13}/k$ ratio for a nematic liquid crystal in nearly homeotropic orientation, in the case in which the intermolecular forces responsible for the nematic phase are due to induced-dipole–induced-dipole interactions.

Let us consider a Cartesian reference frame of the kind used in Sec. II and a nematic molecule just on the surface $(z=0)$ in homeotropic orientation $(\phi=0, \mathbf{n}\|\mathbf{z})$. In this situation Eq. (33) becomes

$$k_1(z=0, \mathbf{n}\|\mathbf{z}) = -\tfrac{1}{4}\sum_{abc}\int_{r_0}^{\infty}\int_0^{2\pi}\int_0^{\pi/2}J_{a,b,c}(r)b(\cos^{a+b-1}\vartheta-\cos^{a+b+1}\vartheta)r^3dr\sin\vartheta d\vartheta\,d\varphi\,,\qquad\text{(A1)}$$

where $\cos\vartheta=\mathbf{n}\cdot\mathbf{u}$. Simple calculations give for k_1 the result

$$k_1(z=0, \mathbf{n}\|\mathbf{z}) = -\tfrac{1}{4}\sum_{abc}J_3(a,b,c)\frac{b}{(a+b)(a+b+2)}\,,\qquad\text{(A2)}$$

where

$$J_3(a,b,c)=4\pi\int_{r_0}^{\infty}J_{a,b,c}(r)r^3dr\,.\qquad\text{(A3)}$$

Expression (A2) holds for a nematic liquid crystal having $\mathbf{n}(0)\|\mathbf{z}$. Let us consider now the case in which $G(\mathbf{n},\mathbf{n'},\mathbf{r})$ is due to the induced-dipole–induced-dipole interaction [28,29]. In this situation the quantities appearing in (31) and (A2) are given by [26]

$$J_{3,4}(a,b,c)=J_{3,4}(\delta_{a0}\delta_{b0}\delta_{c2}-6\delta_{a1}\delta_{b1}\delta_{c1}$$
$$+(9\delta_{a2}\delta_{b2}\delta_{c0})\,,\qquad\text{(A4)}$$

where J_3 or J_4 are constants. By substituting (A4) into (A2) and into the expression (31) giving k_{13} one obtains

$$k_1(z=0,\ \mathbf{n}\|\mathbf{z})=0\,,\qquad\text{(A5)}$$

and hence, from (34) it follows that $k_{\mathrm{DVP}}=0$. Consequently

$$\frac{\bar{k}_{13}}{k}=\frac{k_{\mathrm{DVP}}+k_{13}}{k}=\frac{k_{13}}{k}=-\frac{6}{5}\,.\qquad\text{(A6)}$$

Of course, this result holds only in the case in which the dispersion forces are the most important ones.

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