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► **To cite this version:**

A. Alexe-Ionescu, G. Barbero, Geoffroy Durand. Temperature dependence of surface orientation of nematic liquid crystals. *Journal de Physique II*, 1993, 3 (8), pp.1247-1253. 10.1051/jp2:1993195 . jpa-00247901

**HAL Id: jpa-00247901**

**<https://hal.science/jpa-00247901>**

Submitted on 4 Feb 2008

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Classification  
Physics Abstracts  
61.30 — 68.10

## Temperature dependence of surface orientation of nematic liquid crystals

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(Received 25 February 1993, accepted 7 May 1993)

**Abstract.** — The mixed splay bend curvature elastic constant  $K_{13}$  of nematics is shown to be proportional to  $S$ , the modulus of the quadrupolar orientational parameter. One consequence is presented on the orientation of a nematic on a solid substrate : for an infinitely strong anchoring at an arbitrary angle, the surface energy contribution from  $K_{13}$  gives an apparent surface orientation which depends on the temperature.

### 1. Introduction.

Nematic liquid crystals (NLC) are made by organic molecules of elongated shape [1]. They behave as uniaxial crystals, whose optical axis coincides with the average orientation  $\mathbf{n}$  of the major axes of the molecules forming the phase [2].  $\mathbf{n}$  is called the nematic director. In the absence of external constraints, a solid substrate orients  $\mathbf{n}_s$ , the surface nematic director, along a direction  $\boldsymbol{\pi}$ , known as the easy direction [3]. When  $\mathbf{n}_s \equiv \boldsymbol{\pi}$  for every bulk orientation of  $\mathbf{n}$ , the anchoring is called infinitely strong, otherwise it is finite.

Many experiments have shown that the surface orientation of a uniform NLC sample can depend on the temperature [4-9]. This phenomenon leads even to temperature surface « transitions » when there exists a « critical temperature » above of below which the symmetry of the anchoring is spontaneously broken. Sometimes, the surface orientation keeps changing with the temperature. The temperature surface transitions were firstly interpreted [6] in terms of Parson's [10] or Mada's [11] theories. Phenomenological expressions [12-14] of the surface anchoring energy in term of a power expansion *versus* the modulus  $S$  of the orientational nematic surface order parameter lead already to a temperature ( $T$ ) dependence of the easy orientation at a solid-nematic interface. In this paper we present an alternative interpretation of the temperature change of surface orientation based only on the elastic properties of the NLC.

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The idea is that the mixed splay bend volume curvature elastic constant  $K_{13}$  of nematics depends linearly on  $S$ . Its contribution to the surface anchoring energy depends then on  $T$  differently than the usually accepted surface energies  $\sim S^2$ .

Our paper is organized as follows. In section 2 the usual elastic theory of NLC is recalled. The generalization of the elastic energy density in terms of first and second order spatial derivatives of the tensorial order parameter is given in section 3. The theoretical analysis of the experimental works devoted to detect the temperature variation of the nematic surface orientation is reported in section 4. There we show that the different temperature dependences of the bulk and surface like elastic-constants may be responsible of the change of the nematic orientation induced by the temperature. Finally in section 5 we discuss the physical acceptability of the use of second order derivatives in the elastic energy density.

## 2. Frank-Oseen elastic theory for NLC.

NLC are characterized by a quadrupolar tensor order parameter  $Q$  defined by [15]

$$Q_{ij} = (3/2) S [n_i n_j - (1/3) \delta_{ij}] . \quad (1)$$

In (1)  $n_i$  are the Cartesian components of the NLC director  $\mathbf{n}$ ,  $\delta_{ij}$  are the components of the identity tensor, and  $S$  is the nematic scalar order parameter [16]. In the case in which  $Q$  is position independent, the free energy density of the uniform nematic phase can be written in the Landau-de Gennes form [16], as follows :

$$f_u = (1/2) A_{ijkl} Q_{ij} Q_{kl} + (1/3) B_{ijklmn} Q_{ij} Q_{kl} Q_{mn} + (1/4) C_{ijklmnpq} Q_{ij} Q_{kl} Q_{mn} Q_{pq} , \quad (2)$$

where tensors A, B and C have to be decomposed in terms of the unit tensor of components  $\delta_{ij}$  only. Simple calculations [16] show that  $f_u$  can be put in the form :

$$f_u = (1/2) a(T - T_c^*) Q_{ij} Q_{ij} + (1/3) B Q_{ij} Q_{jk} Q_{ki} Q_{mn} + \\ + (1/4) [C_1 (Q_{ij} Q_{ij})^2 + C_2 Q_{ij} Q_{jk} Q_{kl} Q_{li}] , \quad (3)$$

where  $T_c^*$  is a temperature slightly below the clearing temperature  $T_c$ ,  $a > 0$ ,  $B$ ,  $C_1$  and  $C_2$  are temperature independent. By substituting (1) into (3) one obtains

$$f_u = (3/4) a(T - T_c^*) S^2 + (1/4) B S^3 + (9/16) C S^4 , \quad (4)$$

where  $C = C_1 + (1/2) C_2$ . Expression (4) has been widely used by different authors to analyse the nematic-isotropic phase transition [16].

Let us now suppose that  $Q$  is position dependent, i.e. that the NLC is described by the tensorial field

$$Q_{ij} = Q_{ij}(r) . \quad (5)$$

In this situation  $Q_{ij,k} = \partial Q_{ij} / \partial x_k$  are different from zero. To the non uniformity of  $Q$  it is possible to associate a distortion energy, whose meaning is similar to the elastic density introduced in the classical theory of elasticity [17]. In the first approximation the distortion energy can be expanded in terms of  $Q_{ij,k}$  as [16]

$$f_d(Q_{ij,k}) = f_d(0) + (1/2) K_{ijklmn} Q_{ij,k} Q_{lm,n} , \quad (6)$$

where  $f_d(0) = f_u$  and  $K$  plays the role of elastic tensor. The elastic term of (6), i.e.  $(1/2) K_{ijklmn} Q_{ij,k} Q_{lm,n}$ , contains already a second order term in  $S$ . In this approximation, assuming

also  $S$  to be uniform, the elastic free energy writes :

$$f_c = (1/2) K_{ijklmn} Q_{ij,k} Q_{lm,n} = (1/2) [K_{11} (\text{div } \mathbf{n})^2 + K_{22} (\mathbf{n} \cdot \text{rot } \mathbf{n})^2 + K_{33} (\mathbf{n} \times \text{rot } \mathbf{n})^2], \quad (7)$$

where, in this approximation,  $K_{11} = K_{33} = \alpha S^2$  and  $K_{22} = \beta S^2$ , in which  $\alpha$  and  $\beta$  are temperature independent. Expression (7) has been proposed long ago by Frank and Oseen [18], and it is the fundamental expression of the continuum theory for NLC. The relation  $K_{11} = K_{33}$  holds only near  $T_c$ . In the nematic phase usually  $K_{11} \neq K_{33}$ .

### 3. Nehring-Saupe elastic theory for NLC.

More recently Nehring and Saupe [19] have shown that linear terms in the second order spatial derivatives of  $n_i$  can give a contribution to  $f_d$  of the same order as the quadratic terms in the first order spatial derivatives. This suggests that  $f_d$  has to be considered as a function of  $Q_{ij,k}$  and of  $Q_{ij,\ell\ell}$ . In order to have a well defined variational problem [20], at the second order in  $S$ , expression (6) has to be written [21] as :

$$f_d(Q_{ij,k}, Q_{ij,\ell\ell}) = f_d(0) + (1/2) K_{ijklmn} Q_{ij,k} Q_{lm,n} + N_{ijkl} Q_{ij,\ell\ell} + \\ + (1/2) M_{ijklmnpq} Q_{ij,\ell\ell} Q_{mn,pq} + R_{ijklmnp} Q_{ij,k} Q_{lm,np}. \quad (8)$$

At the second order in  $S$ ,  $K$ ,  $M$  and  $R$  have to be considered temperature independent, i.e. they can be decomposed only in terms of the unit tensor. Furthermore, for NLC, tensor  $R$  is zero because only tensors of even number of indices can be built with the unit tensor. On the contrary, at the same level of approximation for  $f_d$ , the tensor  $N$  has to be decomposed in terms of the unit tensor and of the tensor order parameter  $Q$ . By taking into account that

$$N_{ijkl} = N_{jikl} = N_{ij\ell k} = N_{ji\ell k}, \quad (9)$$

due to the symmetry of  $Q$  and to Schwartz's theorem on the inversion of the spatial derivatives, simple calculations give

$$N_{ijkl} = N_1 \delta_{ij} \delta_{k\ell} + (1/2) N_2 (\delta_{ik} \delta_{j\ell} + \delta_{i\ell} \delta_{jk}) + N_3 \delta_{ij} Q_{k\ell} + \\ + N_4 \delta_{k\ell} Q_{ij} + (1/2) N_5 (\delta_{ik} Q_{j\ell} + \delta_{i\ell} Q_{jk}). \quad (10)$$

As  $Q$  is a traceless tensor (see Eq. (11)),  $N_1$  and  $N_3$  do not contribute to the elastic energy. The elastic term  $N_{ijkl} Q_{ij,\ell\ell}$  is then equivalent to

$$N_{ijkl} Q_{ij,\ell\ell} = N_2 Q_{ij,ij} + N_4 Q_{ij} Q_{ij,kk} + N_5 Q_{j\ell} Q_{ij,i\ell}. \quad (11)$$

It is important to stress that in (11) the first term is linear in  $S$ , whereas the second and the third ones depend on  $S^2$ , as the usual bulk elastic constants. The total energy of a NLC sample, characterized by a strong anchoring on a solid substrate, is obtained by integrating (8) over the volume  $V$  occupied by the NLC. By observing that the r.h.s. of (11) can be rewritten as

$$N_2 (Q_{ij,i}),_j + N_4 (Q_{ij} Q_{ij,k}),_k + N_5 (Q_{j\ell} Q_{ij,i\ell}),_i - [N_4 Q_{ij,k} Q_{ij,k} + N_5 Q_{j\ell,i} Q_{ij,i\ell}], \quad (12)$$

we can conclude that  $N_2$  gives only a surface contribution to the total energy. On the contrary  $N_4$  and  $N_5$  renormalize the bulk energy, quadratic in the first order derivatives of  $Q$ , and furthermore they give also a surface contribution. Both terms connected to  $N_4$  and  $N_5$  are quadratic in the scalar order parameter  $S$ . In conclusion the total elastic energy of the distorted NLC is given by

$$F = \iiint_V f_d(Q_{ij,k}, Q_{ij,\ell\ell}) dV, \quad (13)$$

which, from the above discussion, can be put in the form (13)

$$F = (1/2) \iiint_V [\tilde{K}_{ijklmn} Q_{ij,k} Q_{lm,n} + M_{ijklmnpq} Q_{ij,kl} Q_{mnpq}] dV + \\ + \iint_{\Sigma} [N_2 Q_{im,j} + N_4 Q_{ij} Q_{ij,m} + N_5 Q_{j\ell} Q_{mj,\ell}] \nu_m d\Sigma, \quad (14)$$

where  $\Sigma$  is the surface of  $V$  and  $\nu$  is the unit vector normal to  $d\Sigma$ . In (14)  $\tilde{K}$  is the new elastic tensor connected to the first order spatial derivatives, renormalized by  $N_4$  and  $N_5$ .

By taking into account (1) and that  $\mathbf{n} \cdot \mathbf{n} = 1$ , giving  $n_i n_{i,j} = 0$ , simple calculations give

$$N_2 Q_{im,i} \nu_m = N_2 S (\mathbf{n} \operatorname{div} \mathbf{n} - \mathbf{nX} \operatorname{rot} \mathbf{n}) \nu \\ N_4 Q_{ij} Q_{ij,m} \nu_m = 0 \\ N_5 Q_{j\ell} Q_{mj,\ell} \nu_m = (1/3) N_5 S^2 [2(\mathbf{nX} \operatorname{rot} \mathbf{n}) + \mathbf{n} \operatorname{div} \mathbf{n}] \nu.$$

It follows that  $N_4$  does not give any contribution to the surface energy. The surface term appearing in (14) can be rewritten in the form

$$\iint_{\Sigma} [K_{13} \mathbf{n} \operatorname{div} \mathbf{n} - K_{24} (\mathbf{n} \operatorname{div} \mathbf{n} + \mathbf{nX} \operatorname{rot} \mathbf{n})] \nu d\Sigma$$

where

$$K_{13} = 2 N_2 S + (1/3) N_5 S^2 \quad \text{and} \quad K_{24} = N_2 S + (2/3) N_5 S^2 \quad (14')$$

$K_{13}$  and  $K_{24}$  are the surface like elastic constants introduced by Nehring and Saupe [19]. In what follows, we make the simplifying assumption that we are only dealing with a planar problem in which the  $K_{24}$  contribution is identically zero, and we keep only the usual constant  $K_{13}$ .

#### 4. Temperature dependence surface orientation.

The analysis presented above is valid in general. Let us now consider a particular case in which the NLC sample is a slab of thickness  $d$ . The Cartesian reference frame has the  $z$ -axis normal to the bounding plates, placed at  $z = \pm d/2$ . The  $x$  and  $y$ -axes are then parallel to the two surfaces. Let us suppose furthermore that all physical quantities, like  $\mathbf{n}$ , depend only on the  $z$ -coordinate, and that  $S$  is position independent. All temperature effects are supposed to come from the uniform  $S$  dependent in temperature, from equation (3). Let  $\varphi$  be the angle formed by  $\mathbf{n}$  with the  $z$ -axis, whose value for  $z = \pm d/2$  is  $\Phi$ , imposed by the strong anchoring. In the hypothesis of  $\varphi \ll 1$  (implying  $\Phi \ll 1$  too) expression (14), at the second order in  $\varphi$ , can be rewritten as

$$G = F/\Sigma = \frac{1}{2} \int_{-d/2}^{d/2} \left[ K \left( \frac{d\varphi}{dz} \right)^2 + M \left( \frac{d^2\varphi}{dz^2} \right)^2 \right] dz - \frac{1}{2} K_{13} \Phi \left[ \left( \frac{d\varphi}{dz} \right)_{d/2} - \left( \frac{d\varphi}{dz} \right)_{-d/2} \right] \quad (15)$$

obtained some years ago in a different context [22]. It is important to underline that in (15)  $K$  and  $M$  are proportional to  $S^2$ , whereas  $K_{13} = cS$ , as follows from (14'). From now on the analysis is standard. By minimizing (15) simple calculations give

$$b^2 \frac{d^4\varphi}{dz^4} - \frac{d^2\varphi}{dz^2} = 0, \quad \forall z \in (-d/2, d/2) \quad (16)$$

and

$$b^2 \frac{d^2 \varphi}{dz^2} + R \Phi = 0, \quad z = \pm d/2. \quad (17)$$

In (16)  $b^2 = M/K$  is expected to be temperature independent, whereas in (17)  $R = -K_{13}/K$  is temperature dependent. As shown in reference [22], the symmetric solution of (16), satisfying the boundary conditions (17), is :

$$\varphi(z) = \left[ 1 + R - R \frac{\text{ch}(z/b)}{\text{ch}(d/2b)} \right] \Phi. \quad (18)$$

As discussed in [21, 22]  $b$  is a quasi microscopic length. Consequently  $d/2b \gg 1$ , and hence in the bulk  $\varphi(z)$  is nearly constant and equal to  $\varphi_b$  given by :

$$\varphi_b = (1 + R) \Phi. \quad (19)$$

The surface variation of  $\varphi$  is of the order of

$$\Delta \varphi = \Phi - \varphi_b \sim -R \Phi.$$

Equation (19) can be useful to interpret the temperature dependence of surface orientation. To do this, let us assume that the surface energies involved in the alignment process are very strong and characterized by short range interactions. In this frame  $\Phi$  is fixed by the surface interactions, and can be considered temperature independent. However the physical detectable quantity is not  $\Phi$ , but  $\varphi_b$ , at least in the experimental arrangement of references [4-9]. This quantity for the above discussion, is expected to be temperature dependent. In fact, by taking into account the temperature dependence of  $K_{13} = cS$  and of  $K = \alpha S^2$ , equation (19) can be rewritten as

$$\varphi_b(S) = [1 + (c/\alpha)(1/S)] \Phi. \quad (20)$$

Equation (20) shows that  $\varphi_b$  is temperature dependent. The variation of  $\varphi_b(T)$  depends on the sign of  $c$ , which is not yet known [23]. We underline that the temperature dependence of  $\varphi_b$  follows from the different temperature dependence of  $N = -K_{13}$  with respect to  $K$ . In our analysis this result follows from the tensorial decomposition of  $N$ . In a recent paper Teixeira *et al.* [24], by using a theory of Poniewerski *et al.* [25], have evaluated the ratio between surface and bulk elastic constants. They found that near  $T_c$ , where  $S$  is small,  $R \sim 1/S$ , in agreement with our result.

### 5. On the physical meaning of second order derivatives in $f_e$ .

The use of second order derivatives in the elastic energy density is well known for crystals, as discussed in [21]. Its use in our continuum model leaves open an important question : is it reasonable to use a continuum theory on a scale shorter than  $\xi$ , the coherence length [16] associated with the usual first order derivative elastic term ? One can assume that such a continuous model is acceptable if the characteristic length associated with the second derivative remains larger than a molecular dimension  $\xi_0$ . This length is not exactly  $b$ , since the two (first and second) derivatives must be used together. Let us estimate this length and its temperature dependence. Assume a situation where only the order parameter modulus  $S$  varies in space. This situation is described by the additional bulk free energy density gradient terms

$$\frac{1}{2} K' \left( \frac{dS}{dz} \right)^2 + M' \left( \frac{d^2 S}{dz^2} \right)^2 \quad (21)$$

where  $K'$  and  $M'$  are temperature independent. Equation (21) is obtained by (8), by supposing  $\mathbf{n}$  position independent and furthermore that  $S = S(z)$  only, where  $z$  indicates the distance of the considered point from the wall limiting a semi-infinite sample of NLC. For a small departure  $s$  from the equilibrium value  $s = S(z) - S_b$ , by minimizing the total free energy we obtain the Euler-Lagrange equation

$$M' \frac{d^4 s}{dz^4} - K' \frac{d^2 s}{dz^2} + \frac{df_u}{dS} = 0 \quad (22)$$

where  $f_u$  is given by equation (4). By taking into account that

$$\frac{df_u}{dS} = \left( \frac{df_u}{dS} \right)_{s_b} + \left( \frac{d^2 f_u}{dS^2} \right)_{s_b} s \approx 3 a (T_c - T) s ,$$

equation (22) writes

$$b^2 \xi^2 \frac{d^4 s}{dz^4} - \xi^2 \frac{d^2 s}{dz^2} + s = 0 , \quad (23)$$

where  $\xi^2 = K'/3 a(T_c - T) = \xi_0^2 T/\Delta T$ . It exists now two characteristic lengths, solution of (23), given by :

$$\ell_{\pm}^{-1} = \frac{1}{b} \left( \frac{1 \pm (1 - 4 b^2/\xi^2)}{2} \right)^{1/2} \quad (24)$$

For the  $f$  expansion to be valid, the second derivative term has to be smaller than the first derivative one. This means  $qb < 1$ . This condition is always verified by the two roots (24). For the continuum model to be valid,  $b$  must be larger than the molecular length  $\xi_0$ . The second order elastic constant  $M'$  must be large enough. Then there exists always a temperature  $T_p$  defined by  $2b = \xi(T_p)$  above which the two roots  $\ell_{\pm}^{-1}$  present a complex part. However the  $s(z)$  solution remains stable. If  $M'$  is smaller, i.e. when  $b$  compares with (or is lower than)  $\xi_0$ , the introduction of the second order elasticity is completely useless. Note finally that, close to  $T_c$ , i.e. in the limit of a small  $b/\xi$ , equation (24) predicts  $\ell_+$  of the order of  $b$ , independent of  $T$ , and  $\ell_-$  of the order of  $\xi_0$ . It is interesting to compare this prediction to the experimental finding of the Kent group [26], who could not explain the  $S$  profiles in micropores with a simple exponential decay  $\sim \exp -z/\xi$ . They introduced a surface layer of constant order parameter, and of molecular thickness. This could be related to an adsorption property of the surface, or to the existence of a weak second order derivative elastic constant, with  $b \sim \xi_0$ .

## 6. Conclusion.

In this paper, we have shown from symmetry considerations that the surface elastic constant  $K_{13} \sim cS$ , to second order in  $S$ , whereas the bulk elastic constant  $K$  are proportional to  $S^2$ , to the same order. In this frame by assuming a strong anchoring at the NLC-substrate interface, we have shown that the bulk director orientation is expected to be temperature dependent, in agreement with recent published experimental data. This result depend mainly on the elastic properties of the NLC under consideration, although it can be interpreted in terms of an effective surface energy [27]. Of course other mechanisms, due to the temperature variation of the anchoring energy are possible [28]. Each time a simple exponential relaxation

in the coherence length  $\xi$  is not able to explain the spatial variations of the order parameter modulus  $S$ , one should think of a possible implication of the second order elasticity.

### Acknowledgment.

One of us (A.L.A.I.) thanks I. Dozov, N. Kirov and A. G. Petrov for useful discussions and for the hospitality at the Institute of Solid State Physics of Sofia.

*Note added in proofs* : after our paper was accepted, one of us (A.L.A.I.) has obtained the same result on the  $K_{13}$ -temperature dependence in a mean field approximation (*Phys. Lett. A* **175** (1993) 345).

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