PHYSICAL REVIEW E VOLUME 53, NUMBER 1 JANUARY 1996

Subsurface deformations in nematic liquid crystals

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(Received 9 June 1995; revised manuscript received 8 August 1995)

The existence of subsurface deformations in a nematic liquid crystal sample of finite thickness is considered from a molecular point of view. A lattice approximation is used to take into account the intermolecular interactions responsible for the nematic phase. The analysis shows that for the Maier-Saupe interaction law the director profile is a smooth function in the whole sample. In contrast, in the framework of our simple model, for the induced-dipole–induced-dipole interaction law the director profile presents a large subsurface deformation. The results of our calculation are compared with the elastic theories for nematic liquid crystals recently proposed. In particular it is shown that the intermolecular interactions responsible for the effective splay-bend elastic constant are the origin for the subsurface discontinuity in pretilted nematic liquid crystal samples. Our predictions are obviously limited by the applicability of the naive model considered in the present analysis.

PACS number(s): 61.30.Gd, 61.30.Cz, 61.16.Ch, 81.10.Aj

I. INTRODUCTION

Recently the elastic theory of nematic liquid crystals (NLC) has been the subject of a renewed interest. This is mainly connected with the effect of the surfaces on the NLC orientation in samples of finite volume. Despite the fact that the bulk elastic properties of the NLC are well understood in terms of Frank theory [1], the surface description is far from being complete. The surface contributions to the total free energy f have two sources. One is due to the NLC-substrate interaction f_{SN}, and the other one f_{NN} is an intrinsic property of the NLC. This last term follows from spatial variation of scalar order parameter (f_1), incomplete intermolecular interaction (f_2), and from bulk elastic terms that can be integrated to the surface (f_3) [2]. f_1 takes its origin from the spatial dependence of the NLC elastic constants, due to the fact that they are proportional to the square of the scalar order parameter. f_2 is connected to the reduced symmetry of the NLC phase near the limiting surface. In contrast, f_3 is mainly a bulk elastic term. The contributions f_1, f_2, and f_3 depend on the intermolecular interaction of the NLC phase. Let $g(\vec{\nu},\vec{\nu}',\vec{r})$ be the interaction energy between two NLC molecules in $\vec{R}$ and $\vec{R}'=\vec{R}+\vec{r}$ whose molecular orientations are $\vec{\nu}=\vec{\nu}(\vec{R})$ and $\vec{\nu}'=\vec{\nu}(\vec{R}')$. In general $g(\vec{\nu},\vec{\nu}',\vec{r})$ depends not only on the relative orientation of $\vec{\nu}'$ with respect to $\vec{\nu}$ but also on $(\vec{\nu}\cdot\vec{u})$ and $(\vec{\nu}'\cdot\vec{u})$ where $\vec{u}=\vec{r}/r$. The general expression for $g(\vec{\nu},\vec{\nu}',\vec{r})$ can be written as [3]

$$g(\vec{\nu},\vec{\nu}',\vec{r})=-\sum_{a,b,c}J_{a,b,c}(r)(\vec{\nu}\cdot\vec{\nu}')^a(\vec{\nu}\cdot\vec{u})^b(\vec{\nu}'\cdot\vec{u})^c, \quad (1)$$

where the coupling coefficients depend only on the modulus of $\vec{r}$. By means of Eq. (1) it is possible to recover all the intermolecular interaction laws used until now for NLC [4]. We define intermolecular forces for which $b=c=0$ as being of the first type and those depending also on $(\vec{\nu}\cdot\vec{u})$ and on $(\vec{\nu}'\cdot\vec{u})$ as being of the second type. As shown in [5], f_2 contains an anisotropic part, depending on the NLC orientation, only for intermolecular forces of the second type. On the contrary the f_1 contribution is equivalent to an anisotropic surface energy for both kinds of intermolecular forces [2]. Finally the f_3 term is the sum of the well-known elastic contributions $k_{24}\,\mathrm{div}\,(\vec{n}\,\mathrm{div}\,\vec{n}+\vec{n}\times\mathrm{rot}\,\vec{n})$ and $\overline{k_{13}}\,\mathrm{div}\,(\vec{n}\,\mathrm{div}\,\vec{n})$, where k_{24} is the mixed saddle-splay elastic constant, $\overline{k_{13}}$ is the effective splay-bend elastic constant [6], and $\vec{n}$ is the NLC director defined as the statistical average of $\vec{\nu}$. By using Eq. (1) and operating in a standard manner a simple analysis shows that $\overline{k_{13}}$ is different from zero only for g of the second type [7]. This means that the effective $\overline{k_{13}}$ does not vanish when f_2 contains an anisotropic part. On the contrary k_{24} is different from zero for both kinds of intermolecular forces.

By means of the elastic theory it has been suggested that the $\overline{k_{13}}$ term introduces a strong subsurface distortion in the NLC profile [8–10] proportional to the ratio $\overline{k_{13}}/k$, where k is the usual elastic constant. The analysis performed in [8–10] is well known in the elastic theory of solid materials, as discussed in [11]. Hinov [12] and Pergamenshchik [13] questioned the existence of the subsurface distortion of the NLC orientation. According to them, it is a mathematical artifact and hence it is not physically acceptable. In this paper we want to reconsider the possible existence of a subsurface distortion in NLC by starting directly from the molecular interaction law given by Eq. (1). Our paper is organized as follows. In Sec. II the physical model is described. The total free energy of the system is evaluated in Sec. III for the symmetric and antisymmetric geometry. The main results of the paper are stressed in Sec. IV.

II. PHYSICAL MODEL

The elastic theory is a macroscopic approach. It is valid only in the limit in which the spatial variation of

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1063-651X/96/53(1)/1265(4)/$06.00

the average NLC orientation is very smooth [14]. When a sharp variation of the profile is expected, the elastic description no longer works. However, in order to obtain information about the NLC orientation it is still possible to analyze the problem by means of the total free energy obtained from the intermolecular interaction. We shall show that if g is of the first kind no sharp variation in the NLC profile is found near the boundary. For this kind of interaction law, as underlined above, f_2 reduces to an isotropic term and $\overline{k_{13}} = 0$. On the contrary, if g is of the second type a subsurface sharp variation of the NLC orientation appears. In this situation the anisotropic part of f_2 does not vanish and $\overline{k_{13}} \neq 0$.

In our analysis we shall suppose that the NLC medium may be approximated by a lattice of spacing p (at the end, the limit $p \to \rho$, where ρ is the larger molecular dimension, should be performed). The NLC sample will be assumed to be a slab of thickness $d = Np$ where N is the number of elementary cells along the z axis. Without loss of generality, the director $\vec{n}$ is assumed to be everywhere parallel to the (y, z) plane and $\phi = \arccos(\vec{n} \cdot \vec{z})$ is the tilt angle. For simplicity, $p = 1$ (arbitrary units) and we assume that $\phi = \phi(z)$ only, which is consistent with the slab shape of the sample. The surface NLC orientations are $\phi(\pm d/2) = \Phi$, with Φ being fixed by the surface treatment without conical degeneracy. In other words the substrate-NLC interaction is assumed to be short ranged and very strong with respect to the intermolecular interaction responsible for the NLC phase. This means that $\phi(\pm d/2)$ are independent of the bulk distortions. This hypothesis is reasonable in the cases where the first layer of NLC molecules is fixed by means of chemical bonds much stronger than all interactions considered in our model. Furthermore, the easy axes characterizing the two surfaces are considered to be parallel. In this framework, according to Pergamenshchik-Hinov theory the stable NLC profile is $\phi(z) = \Phi$, $\forall z \in (-d/2, d/2)$. A very simple analysis shows that this is not true, when g is of the second type. In the hypothesis of perfect nematic order, $\vec{\nu}$ coincides with $\vec{n}$ and the total free energy coincides with the total intermolecular interaction energy. This is equivalent to assuming the temperature is $T = 0$. This hypothesis is usually made when the NLC elastic constants are evaluated by means of a semimicroscopic model [3]. However, as is shown in [15], a more realistic calculation, in which the temperature is taken into account, does not change the main results of the simpler model.

III. EVALUATION OF THE TOTAL FREE ENERGY OF THE SYSTEM

The interaction energy between the molecule located at $(0,0,m)$ and the one at (α,β,γ) will be indicated by $g(0,0,m;\alpha,\beta,\gamma)$. The total energy of the molecule in $(0,0,m)$ due to the interaction with all the molecules placed in $m+1 \leq \gamma \leq N/2$ is given by

$$G_{\text{out}}(0,0,m) = \sum_{\gamma=m+1}^{N/2} \sum_{\beta=-\infty}^{\infty} \sum_{\alpha=-\infty}^{\infty} g(0,0,m;\alpha,\beta,\gamma), \tag{2}$$

whereas the one due to the interaction with all the molecules placed in the same plane m is

$$G_{\text{in}}(0,0,m) = \sum_{\beta=-\infty}^{\infty} \sum_{\alpha=-\infty}^{\infty} g(0,0,m;\alpha,\beta,m), \tag{3}$$

in which $\alpha = \beta = 0$ has to be excluded. All the molecules on the same plane are equivalent because of the infinite extension of the sample in the x and y directions with respect to z. Hence the total energy per unit surface on the plane $z = m$ is $F_m = \sigma\,[G_{\text{out}}(0,0,m) + G_{\text{in}}(0,0,m)]$, where $\sigma \propto 1/p^2$ is the molecular surface density, supposed to be uniform. It follows that the total energy of the slab, per unit area, is

$$F = \sigma \sum_{m=-N/2}^{N/2} \sum_{\gamma=m+1}^{N/2} \sum_{\beta=-\infty}^{\infty} \sum_{\alpha=-\infty}^{\infty} g(0,0,m;\alpha,\beta,\gamma) + \sigma \sum_{m=-N/2}^{N/2} \sum_{\beta=-\infty}^{\infty} \sum_{\alpha=-\infty}^{\infty} g(0,0,m;\alpha,\beta,m). \tag{4}$$

From the hypotheses mentioned above, the elements entering the intermolecular interaction energy $g(0,0,m;\alpha,\beta,\gamma)$ are $\vec{n}(0,0,m) = \vec{j}\sin\phi(m) + \vec{k}\cos\phi(m)$ and $\vec{n}(\alpha,\beta,\gamma) = \vec{j}\sin\phi(\gamma) + \vec{k}\cos\phi(\gamma)$ for what concern the NLC directors; $\vec{r}(0,0,m;\alpha,\beta,\gamma) = \alpha\vec{i} + \beta\vec{j} + (\gamma - m)\vec{k}$ for the relative position of (α,β,γ) with respect to $(0,0,m)$. By means of $\vec{r}(0,0,m;\alpha,\beta,\gamma)$ it is possible to define the unit vector $\vec{u}(0,0,m;\alpha,\beta,\gamma) = \vec{r}(0,0,m;\alpha,\beta,\gamma)/r(0,0,m;\alpha,\beta,\gamma)$. In what follows we will consider the intermolecular interaction energy of the kind

$$g(\vec{n},\vec{n}',\vec{r}) = -\frac{C}{r^6}[\vec{n}\cdot\vec{n}' - 3\,\epsilon\,(\vec{n}\cdot\vec{u})(\vec{n}'\cdot\vec{u})]^2, \tag{5}$$

where $C > 0$ and $\epsilon = 0$ or 1. To $\epsilon = 0$ corresponds to the well-known Maier-Saupe law [16], for which $\overline{k_{13}} = 0$ [5] and f_2 is an isotropic contribution. In this case the extended elastic theory [10] predicts no subsurface deformations. To $\epsilon = 1$ corresponds the induced dipole-induced dipole interaction, used for the NLC by Nehring and Saupe [17]. For this kind of interaction, $\overline{k_{13}} \neq 0$ because g depends on $\vec{n}\cdot\vec{u}$ and $\vec{n}'\cdot\vec{u}$ [5]. In the case in which f_2 contains an anisotropic part and $\overline{k_{13}} \neq 0$ the modified elastic theory predicts a subsurface distortion, as discussed in [10].

The profile of the tilt angle will be assumed to be of the kind

$$\phi(z) = \Phi - A + A\frac{\cosh(z/b)}{\cosh(d/2b)}, \tag{6}$$

in the above-mentioned symmetric case with strong anchoring conditions. This is the simpler function describing a subsurface distortion symetrically placed at the boundaries. In Eq. (6) b is a semimicroscopic length, and A a parameter to be determined. By discretizing (6) and substituting it into (5) where $\vec{n} = \vec{n}(0,0,m)$, $\vec{n}' = \vec{n}(\alpha,\beta,\gamma)$, $\vec{r} = \vec{r}(0,0,m;\alpha,\beta,\gamma)$ and

$\vec{u} = \vec{u}(0,0,m;\alpha,\beta,\gamma)$ we obtain $g(0,0,m;\alpha,\beta,\gamma)$. The total free energy per unit surface F is given by (4), and it becomes a function of A. The analysis shows that when $\epsilon = 0$, F reaches its minimum value for $A = 0$. This implies that there is no subsurface distortion. When $\epsilon = 1$ and $\Phi = \pi/4$, F is minimum for $A \approx -0.82$. This means that in this case our simple model predicts a surface distortion.

Instead of assuming for $\phi(z)$ the ansatz (6), remembering the solution deduced by means of the extended elastic theory for the same symmetric problem under consideration [10], we can expand $\phi(z)$ in Fourier's series as follows:

$$\phi(z) = \Phi + \sum_{k=0}^{\infty} C_{2k+1} \cos\left[(2k+1)\frac{\pi}{d}\, z\right], \qquad (7)$$

satisfying the boundary conditions $\phi(\pm d/2) = \Phi$. By substituting (7) into (5) and then into (4), it is possible to deduce the C_{2k+1} coefficients by imposing $dF(C_n)/dC_n = 0$ and $d^2F(C_n)/d{C_n}^2 > 0$ for $n = 1,3,5,\ldots$. For $\epsilon = 0$ the analysis shows that $C_n = 0$ for all n. On the contrary, for $\epsilon = 1$ the profile $\phi(z)$ given by (7), minimizing F is of the kind represented in Fig. 1. From this figure we may derive that (7) is practically coincident with (6) in the bulk. They have the same subsurface distortion. The other differences are not important in the present analysis and they are due only to the slow convergence of (7), because $\phi(z)$ presents a sharp variation near the surface.

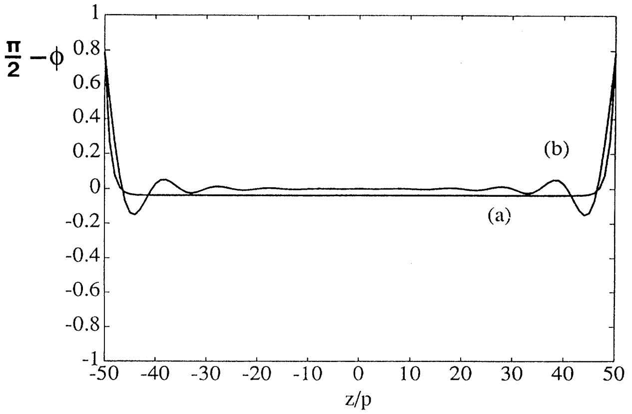

FIG. 1. Tilt angle profile $\phi = \phi(z)$ for $\Phi = \pi/4$. (a) $\phi(z)$ given by the extended elastic theory with the surface distortion $A = -0.82$ minimizing F; (b) Fourier expansion of $\phi(z)$ (with 10 terms) minimizing F.

We stress that the evaluated subsurface distortion is due not only to the $\overline{k_{13}}$ elastic term, but also to the anisotropic part of f_2 [18]. In fact as has been shown in [8], if $\overline{k_{13}}$ alone is responsible for the surface "discontinuity," the parameter A entering in Eq. (6) is

$$A(\overline{k_{13}}) = \frac{1}{2}\frac{\overline{k_{13}}}{k}\sin(2\Phi), \qquad (8)$$

i.e., it depends on $\sin(2\Phi)$. Hence $A(\overline{k_{13}})$ vanishes for $\Phi = 0$ and $\Phi = \pi/2$. On the contrary, our molecular calculations show that A depends on Φ according to the law $A = \Phi - \pi/2$. By taking into account the expression for $A(\overline{k_{13}})$ we deduce that for $\Phi \to 0$, $A(\overline{k_{13}}) \to 0$ whereas $A \to -\pi/2$. This result clearly indicates that the subsurface distortion is due also to the anisotropic part of f_2.

Another interesting situation is the one in which $\phi(\pm d/2) = \pm\Phi$, corresponding to the antisymmetric arrangement of the limiting surfaces. In this case, for $\Phi > \pi/4$ the Pergamenshchik-Hinov theory predicts $\phi(z) = [(\pi - 2\Phi)/d]\, z + \pi/2$. In order to check the possible existence of a subsurface deformation, let us consider a $\phi(z)$ profile of the kind [10]

$$\phi(z) = \frac{\pi - 2(\Phi + A)}{d}\, z + \frac{\pi}{2} + A\frac{\sinh(z/b)}{\sinh(d/2b)}, \qquad (9)$$

which reduces to a Hinov-Pergamenshchick one for $A = 0$. By operating in the same way as before, we can determine the A coefficient minimizing the total energy when $g(\vec{n},\vec{n}',\vec{r})$ is given by (5). For $\epsilon = 0$ and $\Phi = \pi/3$, A is very small (≈ 0.02), whereas for $\epsilon = 1$ it is rather large ($A \approx 0.6$). In the frame of the elastic theory the $A \neq 0$ even in the case $\epsilon = 0$ is due to the positional dependence of the elastic constant [2]. This means that also in the antisymmetric case, according to our naive model, the surface distortion is mainly connected to the anisotropic part of f_2 and to the splay-bend elastic constant. Again, instead of using (9) we can expand $\phi(z)$ in Fourier's series. By minimizing the total energy given by (4) with respect to the expansion coefficients, we obtain a profile almost coincident with (9).

It is possible to apply our model to interaction laws obtained by superposing, in a suitable manner, the Maier-Saupe $g_{\rm MS}$ and the induced-dipole–induced-dipole g_{NS} interaction. In this case the effective interaction could be written as $g(\vec{n},\vec{n}',\vec{r}) = [w_1 g_{\rm MS}(\vec{n},\vec{n}',\vec{r}) + w_2 g_{NS}(\vec{n},\vec{n}',\vec{r})]/(w_1 + w_2)$. The analysis shows that for $w_1 \gg w_2$ the surface distortion decreases, but still exists. For the symmetric case $\phi(\pm d/2) = \Phi = 2\pi/9$ and $w_1 = 10\,w_2$, or $w_1 = 100\,w_2$ the minimizing values are $A = -0.9$ and $A = -0.65$, respectively. This means that A decreases when w_2/w_1 decreases, as expected. The same calculation may be performed by considering other cases of intermolecular forces giving rise to the NLC phase [15].

IV. CONCLUSIONS

From the results reported above we can infer that a subsurface distortion localized over a semimicroscopic length b of the order of few molecular dimensions exists when the interaction energy g is of the second type. Hence, in this boundary layer the usual elastic theory cannot be applied and the usual bulk Frank elastic energy density has to be modified. This can be done by including terms in the square of the second-order derivatives of $\vec{n}$, as it has been proposed in [10]. Otherwise, the problem is ill posed, and it cannot be solved in the frame of continuous functions [9]. If this approach is considered not justified from a fundamental point of view, it is possible to modify the surface free energy including in it also the destabilizing effect of the $\overline{k_{13}}$ term and of the anisotropic part of f_2, as suggested in [19].

The particular interaction energy considered by us, i.e., the induced-dipole–induced-dipole interaction, for a symmetric arrangement, is such that (i) in the bulk the NLC is not very far from the planar orientation everywhere and (ii) a large subsurface distortion is present near the limiting walls. By taking into account that bulk tilted NLC samples can be easily made, we can deduce that this kind of interaction is, probably, not the most important for the formation of the NLC phase. In other words, this means that even though this interaction is always present, other interactions play a more important role in giving rise to the nematic phase. For this reason recent papers (Ref. [15], and references therein) devoted to the determination of the elastic constants by means of statistical mechanics methods consider other kinds of intermolecular potentials. An analysis of the importance of the induced-dipole–induced-dipole in the NLC phase is beyond the aim of this paper. A surface distortion is, however, connected to this interaction. This distortion disappears in the case of planar surface alignment. From these results we can conclude that a surface deformation can appear for intermolecular forces of the second type. Such a surface distortion has been experimentally detected by Guyot-Sionnest, Siung, and Shen [20] by means of the second harmonic generation technique. Our analysis furthermore shows that, in general, the molecular alignment in the bulk of a NLC sample is different from that of the first monolayer, and it is not solely determined by the latter. The model presented in this paper is very simple and its predictions are limited to its applicability domain. However it shows that a subsurface deformation can exist, although its real amplitude is probably not so large as evaluated by us. To estimate it in a correct manner the calculations presented in our paper should be performed without the lattice approximation, or else other kinds of randomness of the nematic molecules on the lattice planes should be introduced. This is necessary because a lattice approximation introduces easy directions parallel to the crystallographic axes. An analysis of this kind is in progress [21]. It confirms the main results obtained in our paper, but the surface "discontinuity" is smaller than the one evaluated by us.

ACKNOWLEDGMENTS

Many thanks are due to C. Oldano (Torino) and T. J. Sluckin (Southampton) for useful discussions. One of us (L.R.E.) acknowledges the financial support of INFM (Italy) and CAPES (Brazil).

[1] F. C. Frank, Discuss. Faraday Soc. **25**, 19 (1958).

[2] A. L. Alexe-Ionescu, R. Barberi, G. Barbero, and M. Giocondo, Phys. Rev. E **49**, 5378 (1994).

[3] G. Vertogen, Physica (Amsterdam) **117A**, 227 (1983).

[4] G. Vertogen, S. D. P. Flapper, and C. Dullemond, J. Chem. Phys. **76**, 616 (1982).

[5] G. Barbero and C. Oldano, Mol. Cryst. Liq. Cryst. **170**, 99 (1989).

[6] R. Barberi, G. Barbero, M. Giocondo, and R. Moldovan, Phys. Rev. E **50**, 2093 (1994).

[7] G. Barbero and R. Barberi, in *Physics of Liquid Crystalline Materials*, edited by I. C. Khoo and F. Simoni (Gordon and Breach, Philadelphia, 1990), Chap. VIII.

[8] G. Barbero and G. Durand, Phys. Rev. E **48**, 345 (1993).

[9] C. Oldano and G. Barbero, Phys. Lett. **110A**, 213 (1985).

[10] G. Barbero, N. V. Madhusudana, and C. Oldano, J. Phys. (Paris) **50**, 2263 (1989).

[11] J. F. Nye, *Physical Properties of Crystals* (Clarendon, Oxford, 1957).

[12] H. P. Hinov, Mol. Cryst. Liq. Cryst. **178**, 53 (1990).

[13] V. M. Pergamenshchik, Phys. Rev. E **48**, 1254 (1993).

[14] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

[15] P. I. C. Teixeira, V. M. Pergamenshchik, and T. J. Slukin, Mol. Phys. **80**, 1339 (1993).

[16] W. Maier and A. Saupe, Z. Naturforsh. **15A**, 287 (1960).

[17] J. Nehring and A. Saupe, J. Chem. Phys. **54**, 337 (1971); **56**, 5527 (1972).

[18] E. Dubois-Violette and P. G. de Gennes, J. Phys. (Paris) Lett. **36**, L255 (1975); J. Colloid Interface Sci. **57**, 403 (1976).

[19] G. Barbero, Z. Gabbasova, and A. Yu. Kosevich, J. Phys. II (France) **1**, 1505 (1991).

[20] P. Guyot-Sionnest, H. H. Siung, and Y. R. Shen, Phys. Rev. Lett. **57**, 2963 (1986).

[21] P. Galatola, C. Oldano, and M. Rajteri, Phys. Lett. A (to be published).