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Nematic liquid crystal anchoring on Langmuir–Blodgett films: steric, biphilic, dielectric and flexoelectric aspects and instabilities*

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Abstract. A survey of the published data on the type of anchoring (homeotropic, planar or tilted) of nematic liquid crystals on Langmuir–Blodgett (LB) films of charged and dipolar amphiphiles, as a function of surface density of molecules and number of molecular layers in the film, reveals a complex and seemingly controversial picture. A theoretical model of the anchoring, taking into account the non-homogeneous electric field originating from surface charges and dipoles, which dictates the liquid crystal orientation via a competition of dielectric, flexoelectric and ordoelectric torques, predicts a rich variety of anchoring states, depending on the sign of surface charges, the orientation of surface dipoles and the signs of dielectric anisotropy and total flexocoefficient. In specific situations, critical molecular densities and thicknesses for anchoring transitions (either first or second order) from homeotropic to tilted to planar or *vice versa* are predicted. ‘Reentrance’ sequences, homeotropic–planar–homeotropic and planar–homeotropic–planar, are also possible, while surface density increases monotonically. Thus, the model resolves the apparent contradictions between various experiments and puts them in a general framework for the first time.

1. Introduction

Langmuir–Blodgett (LB) films are organized molecular films deposited on solid substrates by the method of Langmuir and Blodgett, i.e. by means of transferring an amphiphilic molecular monolayer of controlled density formed at an air–water interface over a solid support being slowly pulled (or pushed) normally through the interface. This procedure can be repeated many times. Thus a multilayer can result. Either charged or dipolar amphiphiles can be employed. Deposition is usually carried out in a centrosymmetric manner (Y type), but with certain substances polar LB films can be built up, facing the substrate either with hydrophobic tails (X type) or with hydrophilic heads (Z type).

The first experimental studies of the interaction of LB films with nematic liquid crystals (NLCs) were initiated in 1978 [5–7]. Still earlier, the mode of anchoring of the nematic director on self-assembled amphiphilic monolayers, obtained by dipping the substrates in surfactant solutions, was studied [1–4], both experimentally and theoretically (using a thermodynamic approach in terms of interfacial surface tension). A shortcoming of the self-assembled films is that their surface density is usually not known and could

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hardly be controlled, although a dependence on the volume concentration is to be expected. The elegant work of Proust and Ter-Minassian-Saraga [1], providing a direct measure of this density by measuring the surface radioactivity of a labelled surfactant, cetyltrimethylammonium bromide (CTAB), is still the only one of this type. Nevertheless, qualitative observations of the variation of anchoring on self-assembled films of variable surface density are possible in a concentration gradient of the surfactant, e.g. lecithin [8].

Since then, a number of papers [9–19] have been published, emphasizing, in particular, the mode of nematic anchoring on multilayer LB films and its dependence on the number of layers [9, 10, 11, 13], the temperature-driven anchoring transitions [14, 17, 18] and the theory [9, 13, 14, 19].

Let us now briefly summarize the experimental findings. In the case of a positively charged CTAB monolayer on glass and nematic MBBA, a critical surface density of $9 \times 10^{17} \text{ mol m}^{-2}$ was found, with planar director anchoring below this density switching to homeotropic above it [1–3]. This finding was qualitatively confirmed with egg lecithin film having a surface density gradient in contact with MBBA [8]. With LB monolayers of dilauroyl lecithin (a non-charged, dipolar lipid with two alkyl chains) a critical area per molecule close to 0.75 nm^2 , i.e. surface density of $1.3 \times 10^{18} \text{ mol m}^{-2}$, was observed; this time however the nematic PCH7 (heptylcyanophenylcyclohexane) was found to switch from homeotropic to irregular tilted alignment, the tilt angle increasing with packing density [6]. Since then it has been widely believed that the steric forces due to the presence of holes in the non-compact monolayer are of paramount importance for the homeotropic anchoring, and that compact monolayers had no orienting action. However, in 1985 it was demonstrated [11] that very compact monolayers of ω -tricosenoic acid on indium thin oxide electrodes (surface densities up to $5 \times 10^{18} \text{ mol m}^{-2}$) can still orient a variety of liquid crystals, e.g. E7 (a BDH mixture of cyanobiphenyls) almost homeotropically (4° off the normal). The homeotropic alignment of MBBA by dipalmitoyl lecithin monolayers was found to disappear below $0.8 \text{ nm}^2 \text{ mol}^{-1}$, i.e. above $1.25 \times 10^{18} \text{ mol m}^{-2}$, but even more compact monolayers with $\geq 2 \times 10^{18} \text{ mol m}^{-2}$ still induced a tilted homeotropic alignment of 8CB (octylcyanobiphenyl) [16].

The experimental data on thickness dependence of anchoring in monolayer and multilayer LB films do not provide a simple pattern either. By varying the chain length of aliphatic monoamines layers on glass Porte [4] found a critical length of 11 CH_2 groups ($\sim 1.4 \text{ nm}$) above which the anchoring is homeotropic, while below it is tilted, the tilt angle increasing with decreasing chain length. Blinov *et al* [9, 10], using an LB film staircase on crystalline mica (with anisotropic van der Waals orienting action) found a local Fredericksz transition [20] from planar to homeotropic anchoring above a critical thickness of 15 nm for MBBA and 50 nm for 5CB using centrosymmetric Y films of stearic acid. With polar X films of the same compound the critical thickness for MBBA exceeded 50 nm, while for 5CB it was very small (less than 5 nm).

Contrary to these findings, Saunders *et al* [11] found a transition from (nearly) homeotropic to tilted orientation of E7 on ω -tricosenoic acid and Cd arachidate on ITO by changing from one to three monolayers (i.e. a critical thickness of two monolayers). Similarly, Grosperin [13] found a critical thickness of four monolayers of behenic acid on glass for an anchoring transition of 5CB from homeotropic to planar, this transition being very abrupt (from exactly 0° at three layers to $65\text{--}70^\circ$ off the normal at five layers, this angle only slightly increasing up to 80° at 30 LB layers).

As we can see, no picture of sufficient generality is emerging from the available experimental data. On the contrary they look contradictory, leaving the reader with some degree of confusion.

Several attempts for theoretical modelling have been made so far, starting with the thermodynamic argument of Greagh and Kmetz [21], later refined by Proust and Ter-Minassian-Saraga [3] and by Porte [4] to explain the tilted orientation as well. This argument essentially predicts a planar anchoring when the LC wets the surface and a homeotropic one in the case of non-wetting. However, as underlined by Porte [4], while the relative importance of permanent dipolar forces at the interface and the steric effects of aliphatic chains is not measured, quantitative agreement with interfacial surface tension data will not be very significant. The importance of surface electric field coupling to dielectric anisotropy of NLCs was recognized by Blinov *et al* [9, 10]. A tilt instability in the LB film itself, similar to the SmA–SmC transition under pressure, was predicted by Alexe-Ionescu *et al* [19] as due to the electric force from the surface charges. However, no attention was paid until now to the non-homogeneous character of the surface electric field and the possible coupling of the field gradient to the quadrupolar NLC density via the gradient flexoelectric effect [22–24].

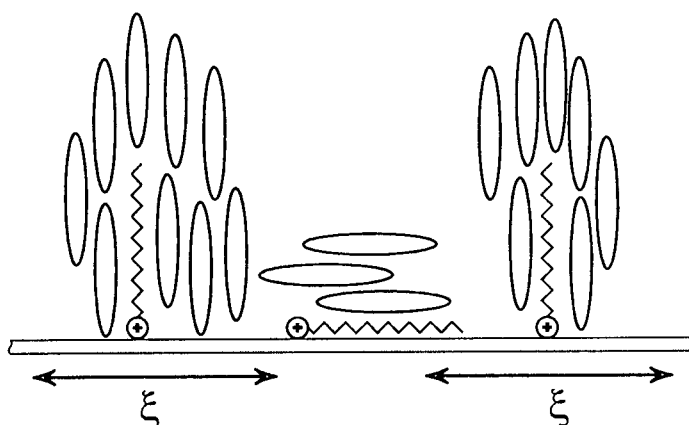


Figure 1. Steric aspect of the homeotropic and planar orientation of nematic molecules by surfactant molecules with different surface orientation at low surface density. A nematic cluster of size ξ , the correlation length of the order parameter, extends around each surfactant molecule.

As we will see below, the explicit account of gradient flexoeffect introduces another material constant of the nematic, its total flexocoefficient, into the description, thus allowing for a much richer possibility of anchoring situations. It was recently mentioned by Strigazzi *et al* [14] that in a complete description the elastic anisotropy, flexoelectricity and order electricity close to the substrate should be taken into account. Order electricity effects have already been discussed [13].

2. Theory

Let us consider a glass substrate covered with an LB monolayer or multilayer film of amphiphilic molecules (see figures 1 and 2). These molecules could be either charged or dipolar, or both. Following the LB deposition procedure, the last LB monolayer in Y deposition mode usually has its hydrophobic tails outward, facing the NLC. We assume that the tails are nearly perpendicular to the interface, although tilted arrangements are also possible. Very important for our model is the fact that near the solid substrate an exponentially decaying electric field is present, due to the double layer created by the charges or the residual field of point dipoles.

For symmetry this electric field is normal to the bounding surface and its modulus depends on the distance of the considered point from the surface. We use a Cartesian

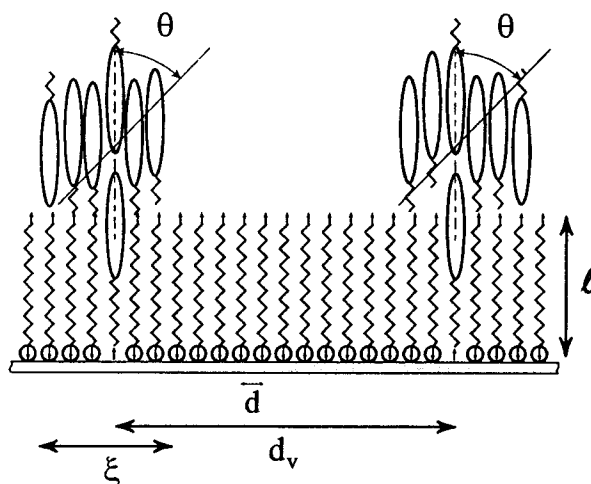


Figure 2. Steric and biphilic aspects of homeotropic anchoring of nematics on a high-surface-density LB film. Nematic molecules possessing a biphilic asymmetry of the end substituents are trapped in monolayer vacancies in a polar fashion. A cluster of size ξ is oriented by each vacancy. d_v is the distance between vacancies; d is the intermolecular distance; l is the monolayer thickness; μ is the dipole moment of the head group; methyl end groups' dipoles are also shown. If the head group dipolar field is strong enough, a localized tilt instability can occur around each vacancy due to the gradient flexoelectric coupling (see the text and figure 5).

reference frame having the z -axis normal to the surface and directed toward the NLC. In this frame the electric field is $\mathbf{E} = E(z)\mathbf{k}$, where \mathbf{k} is the unit vector of the z -axis. The electric field \mathbf{E} acts on the NLC. Let us suppose that (i) the nematic average orientation is constant across the sample, i.e. that the nematic director \mathbf{n} is position independent, (ii) \mathbf{n} is everywhere parallel to the (x, z) plane and (iii) all physical quantities are x and y independent.

In this frame the total energy per unit area of the NLC is given by

$$F = - \int_0^\infty \left\{ \frac{1}{2} \Delta \varepsilon E_i N_{ij} E_j + e N_{ij} E_{i,j} \right\} dz + \frac{1}{2} W k_i N_{ij} k_j \quad (1)$$

where

$$N_{ij} = \frac{1}{2} [n_i n_j - \frac{1}{3} \delta_{ij}] \quad (2)$$

is the tensor order parameter. In (1) the first term represents the dielectric interaction and $\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ is the dielectric anisotropy. The second term is the quadrupolar contribution to the electrostatic interaction energy. This is typical of nematic materials, because they are ferroelectric quadrupolar media. The electrostatic energy is delocalized over the layer in which $E(z)$ is different from zero. In the case of charged amphiphiles the thickness over which the field is delocalized coincides with the Debye screening length. With point dipoles in a plane square lattice with a lattice constant d this thickness is $d/2\pi$.

The latter term present in (1) takes into account the short-range interaction between the NLC and the substrate, due, for instance, to van der Waals forces. W is the so-called anchoring strength. $W < 0$ means that the easy direction is homeotropic to the substrate.

It is well known [5] that amphiphilic monolayer anchoring is strongly dependent on surface density. Expanded layers in general give much better homeotropic orientation than compressed ones. This was explained in terms of a steric interaction model by Hiltrop and Stegemeyer [5] in which LC molecules penetrate the holes in the LB monolayer. To give a quantitative expression of this idea we propose the following functional dependence of the steric component of the anchoring energy:

$$W_s = W_0(n/n_m)(1 - n/n_m) \quad (3)$$

where n is the actual surface density and n_m is the maximal possible surface density at close packing ($n_m \simeq 5 \times 10^{18} \text{ mol m}^{-2}$ for saturated fatty acids with hydrocarbon chain cross section of 0.20 nm^2).

This expression will be used to discuss the orienting action of monolayers at different surface density. In the case of multilayered LB films, whose deposition is as a rule performed with closely packed monolayers, the steric component of the anchoring energy is probably very low, and in any case a constant. Some time variation cannot be excluded, though, as a gradual dissolution of molecules from the outermost monolayer into the LC is quite probable, leading to a slow increase with time of W_s .

The total anchoring energy W of the NLC may contain also van der Waals contributions W_{vdw} from the orientational interactions, substrate–NLC and LB–NLC. The substrate–NLC contribution is usually screened by increasing the LB film thickness [9] while the LB–NLC is probably enhanced.

Denoting the tilt angle by $\theta = \cos^{-1}(\mathbf{n} \cdot \mathbf{k})$, (1) becomes

$$F = \frac{1}{2} \left\{ - \int_0^\infty \left[\frac{\Delta\epsilon}{2} E^2(z) - e \frac{dE}{dz} \right] dz + \frac{W}{2} \right\} \left(\cos^2 \vartheta - \frac{1}{3} \right). \quad (4)$$

In the hypothesis in which

$$E(z) = E_0 e^{-z/\lambda} \quad (5)$$

where λ is some typical length (Debye screening length),

$$F = \frac{1}{2} \left\{ - \left(\frac{1}{4} \lambda \Delta\epsilon E_0 + e \right) E_0 + W \right\} \left(\cos^2 \vartheta - \frac{1}{3} \right). \quad (6)$$

(6) shows that according to the value E_0 of the surface field, the easy tilt angle imposed by the substrate is homeotropic or planar. The critical fields for the surface phase transitions are given by

$$E_{1,2} = -2 \frac{e}{\lambda \Delta\epsilon} \{ 1 \pm \sqrt{1 + W \lambda \Delta\epsilon / e^2} \}. \quad (7)$$

First we will consider the case of multilayer LB films. In this case the surface density of molecules in the outer layer is fixed (apart from a slow decrease with time, see above), so can be considered as constant. Nevertheless, an independent variation of total surface charge density and thus the surface field is possible by increasing the number of charged monolayers.

Equation (6) shows the following.

(i) If $W = 0$ (e.g. $n = n_{\max}$), i.e. no direct interaction between the nematic and LB film exists.

$$E_1 = 0 \quad E_2 = -4e/(\lambda\Delta\epsilon). \quad (8)$$

Four possible types of anchoring for the most studied NLCs MBBA ($\Delta\epsilon < 0$, $e < 0$) and 5CB ($\Delta\epsilon > 0$, $e > 0$) on positively and negatively charged LB films are summarized in figure 3. Let us note that another two combinations of signs ($\Delta\epsilon > 0$, $e > 0$) and ($\Delta\epsilon < 0$, $e > 0$) are in principle possible for NLC materials, thus making the total number of anchoring types equal to eight. When dielectric and gradient flexoelectric torques act in concert, they would stabilize the homeotropic or planar anchoring at any value of the electric field, i.e. at any surface charge or dipolar density. In contrast, when they are in competition, a surface phase transition at a critical field is predicted. The gradient flexoelectric torque, being linear in surface density, always dictates the anchoring in the low-density region, being overcome by the dielectric torque above the critical value.

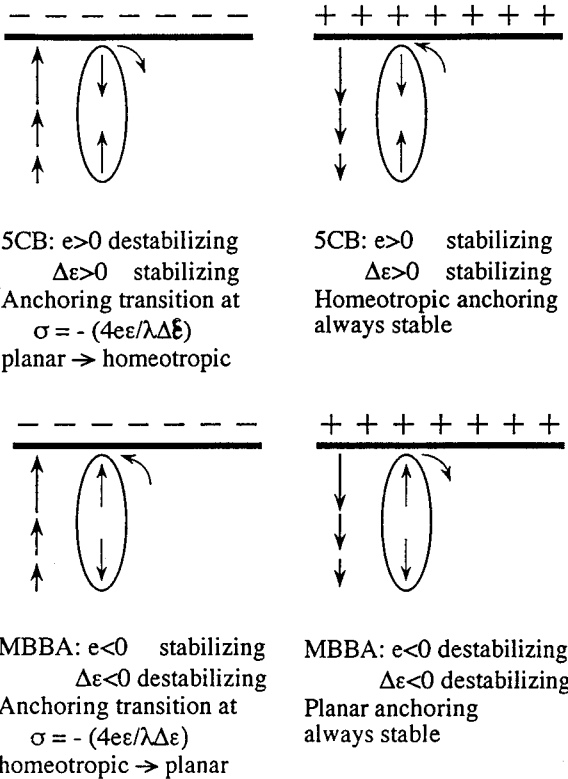


Figure 3. Four basic types of anchoring of 5CB and MBBA on positively and negatively charged LB films and anchoring transitions between them.

(ii) If $W < 0$ (the surface alone tries to impose homeotropic alignment), but $\Delta\epsilon > 0$ and $e > 0$, and furthermore $|W| < (e^2/\lambda\Delta\epsilon)$, the phase diagram is that shown in figure 4(a). In contrast, for $|W| > (e^2/\lambda\Delta\epsilon)$ the planar orientation is never stable. Other cases can be considered according to the signs of e and $\Delta\epsilon$.

(iii) If $W > 0$ (the surface alone tries to impose planar alignment), but $\Delta\epsilon > 0$ and $e > 0$, the phase diagram is of the kind shown in figure 4(b).

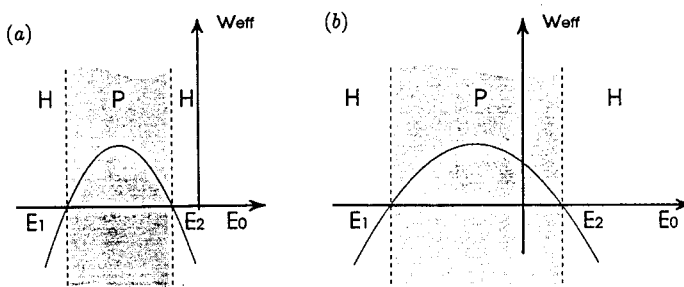


Figure 4. Phase diagrams showing the NLC orientation versus the surface field E_0 . W_{eff} is the effective surface anchoring energy defined by $W_{\text{eff}} = -[\frac{1}{4}\lambda\Delta\epsilon E_0 + e]E_0 + W$ (see (6)), taking into account the short-range part W and the electrostatic contribution. $W_{\text{eff}} < 0$ implies that the homeotropic orientation is stable; $W_{\text{eff}} > 0$ that the planar orientation is stable. (a) $W < 0$ (the short-range part tends to induce homeotropic alignment), $\Delta\epsilon > 0$, $e > 0$ and $|W| < e^2/\lambda\Delta\epsilon$. In this case, for $E_1 < E < E_2$, the stable orientation is the planar one. For $|W| > e^2/\lambda\Delta\epsilon$ the planar orientation is never stable. (b) $W > 0$ (the short-range part tends to induce planar alignment), $\Delta\epsilon > 0$, $e > 0$. In this case for every W the planar orientation may be stable if the surface field is in the range (E_1, E_2) .

It is important to underline that in the cases considered the surface transition from one state to another one is abrupt, i.e. from $0 \rightarrow \pi/2$ or *vice versa*. In the simple case in which E_0 is due to the surface charge density of the molecules

$$E_0 = \sigma/\epsilon \quad (9)$$

where ϵ is an average dielectric constant of the NLC, (6) gives the critical surface densities for the orientation transitions.

Until now we have neglected the dielectric energy due to the order–electric effect [13]. By taking into account this contribution (6) becomes

$$F = A(\cos^2 \theta - \frac{1}{3}) + B(\cos^2 \theta - \frac{1}{3})^2 \quad (10)$$

where

$$A = \frac{1}{2}\{-[\frac{1}{4}\lambda\Delta\epsilon E_0 + (1 + \Delta S)e]E_0 + W\} \quad (11)$$

and

$$B = [(\Delta S)^2/2\epsilon\xi]e^2. \quad (12)$$

In (11) the scalar order parameter varies in the surface layer of thickness ξ (the nematic coherence length). $\Delta S = S_b - S_s$ is the surface variation of scalar order parameter.

From (10) simple calculations give

$$dF/d\vartheta = -\{A + 2B(\cos^2 \theta - \frac{1}{3})\} \sin(2\theta) \quad (13)$$

and

$$d^2F/d\vartheta^2 = -2\{A + 2B(\cos^2 \vartheta - \frac{1}{3})\} \cos(2\vartheta) + 2B \sin^2(2\vartheta). \quad (14)$$

It follows that the solutions of $dF/d\vartheta = 0$ are

$$\vartheta_1 = 0 \quad \vartheta_2 = \pi/2 \quad \cos^2 \vartheta_3 = (\frac{1}{3}) - (A/2B). \quad (15)$$

Solution ϑ_3 exists only if $0 \leq \cos^2 \vartheta_3 \leq 1$, giving

$$-\frac{4}{3} < A/B < \frac{2}{3}. \quad (16)$$

The homeotropic solution ($\vartheta_1 = 0$) is stable for

$$(d^2 F/d\vartheta^2)_{\vartheta_1=0} = -2(A + \frac{4}{3}B) > 0 \quad (17)$$

$$A < -4/3B \quad (18)$$

which is equivalent to a condition on the surface field (and hence on the surface charge density from (11)).

The planar solution ($\vartheta_2 = \pi/2$) is stable for

$$(d^2 F/d\vartheta^2)_{\vartheta_2=\pi/2} = +2(A - \frac{2}{3}B) > 0 \quad (19)$$

i.e.

$$A > \frac{2}{3}B. \quad (20)$$

The tilted orientation (ϑ_3) is stable when (16) holds.

3. Discussion

3.1. Anchoring on charged monolayers with variable surface density

First, we will analyse the planar–homeotropic transition in the MBBA–CTAB system, taking place at $n_{cr}/n_m = 0.18$. As this is the region of low surface coverage, we can neglect the term $(1 - n_m)$ in the $W_s(n)$ dependence. Also, we need to relate surface charge density σ , or the surface field E_0 , to the amphiphile density n . We observe that if the sign of surface charge is that of CTAB (i.e. positive) no anchoring transition with MBBA would be possible, because both $\Delta\epsilon$ and e torques promote planar anchoring (figure 3). This is why we have to assume a negative surface charge due to a selective adsorption of CTAB counterions over the *available free area* not covered by CTAB molecules, while the CTAB head group charge is fully compensated. Separate experiments performed by us (to be published elsewhere) *do indicate* that the surface charge sign in this system is, indeed, negative.

$$\sigma = \beta q_e (n_m - n) \quad (21)$$

where β is a screening coefficient allowing for a partial screening of the surface charges, q_e is the elementary charge (in this case negative). The threshold condition for the density will then read ($W_0 < 0$ for homeotropic orientation)

$$-(\frac{1}{4}\lambda\Delta\epsilon\beta q_e(n_m - n)/\epsilon + e)\beta q_e(n_m - n)/\epsilon - |W_0|(n/n_m)(1 - n/n_m) = 0. \quad (22)$$

In a first approximation we neglect the anchoring energy term altogether. Taking into account the fact that $\Delta\epsilon < 0$ and $e < 0$ for MBBA and also $q_e < 0$, we obtained a solution for n_{cr} :

$$n_{cr}/n_m = 1 - 4|e|\epsilon A_m/\lambda|\Delta\epsilon||q_e|\beta \quad (23)$$

where $A_m = 1/n_m$ is the minimal area per CTAB molecule at close packing. Taking $A_m = 0.2 \text{ nm}^2$, i.e. $n_m = 5 \times 10^{18} \text{ mol m}^{-2}$, with $q_e = 1.6 \times 10^{19} \text{ C}$, and MBBA material parameters as follows: $e = -2 \times 10^{11} \text{ C m}^{-1}$ [24], $\Delta\epsilon = -0.7\epsilon_0$, $\epsilon = 5\epsilon_0$, $\epsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$, and assuming $\lambda = 1 \times 10^{-7} \text{ m}$ (typical for a weakly conducting LC) we can see from (23) that the flexoelectric term could overcome the planar action of the dielectric anisotropy term in the low-coverage range only at very low β , i.e. at strong screening. If $\beta = 1$, then $n_{cr}/n_m = 1.7 \times 10^{-3} \simeq 1$. On the other hand β has a lower limit, below which the anchoring will always be homeotropic:

$$\beta > 4|e|\epsilon A_m/\lambda|\Delta\epsilon||q_e| = 7.1 \times 10^{-3}. \quad (24)$$

Assuming then $\beta = 8.7 \times 10^{-3}$, we could calculate from (23) $n_{cr}/n_m = 0.18$, in agreement with experiment. This calculation shows that the charge effects are very powerful and even one elementary charge per 10^2 molecules suffices to induce a surface transition.

Now, if a homeotropic anchoring energy term ($W_0 < 0$) is considered in (22) the critical density (23) would be reduced, i.e. a reduction of the screening would be necessary to keep the solution of (22) in accordance with experiment. If, on the other hand, the anchoring energy favours a planar orientation (e.g. due to CTAB molecules on the surface in the low-coverage range) then larger screening (smaller β) would be necessary. In principle, it is possible to discuss this planar-homeotropic transition in steric terms only, i.e. by an anchoring energy dependence that changes its sign due to the change of the orientation of adsorbed molecules from planar to homeotropic by increasing the coverage [1]. Such situations, involving internal reorientation of the LB film itself, will be the object of our future work. In a crude steric model we could predict a critical density $(n_{cr}/n_m) = 2/(1 + l/d)$, where l is the length and d is the width of the surfactant molecule. For CTAB ($l \simeq 2.2 \text{ nm}$, $d \simeq 0.45 \text{ nm}$) we calculate $n_{cr}/n_m = 0.34$, which is a factor of two too high. That means that a negative surface charge density will in any case be necessary to bring the critical density down to the experimental level.

Let us now discuss the homeotropic-planar (or tilted) transition on compact lecithin monolayers. Here we are in a position to put the term $(n/n_m) \simeq 1$ to simplify the equation. We shall also assume a small partial electric charge per lecithin head group, due e.g. to the fact that pH of the water subphase does not exactly match the isoelectric point of the phosphocholin zwitterion, i.e. $\beta \neq 0$, $\beta \ll 1$. In such a case we obtain from (22)

$$(\lambda/4)(\Delta\epsilon/\epsilon)[(\beta q_e n_m)^2/\epsilon_0](n/n_m)^2 + (e\beta q_e n_m/\epsilon_0 - |W_0|)(n/n_m) + |W_0| = 0. \quad (25)$$

For lecithin $n_m = 2 \times 10^{18} \text{ mol m}^{-2}$, $A_m = 0.5 \text{ nm}^2$. With the above quoted values of material constants of MBBA (or of PCB: $e = +2 \times 10^{11} \text{ C m}^{-1}$, $\Delta\epsilon = 14\epsilon_0$, $\epsilon = 10\epsilon_0$) and $\beta \sim 10^{-1}$ the first term in (25) is negligible. Then a simple solution for the critical density follows:

$$n_{cr}/n_m = (1 - (e/\epsilon_0)\beta q_e/|W_0|A_m)^{-1}. \quad (26)$$

In order to have a meaningful solution $(n_{cr}/n_m) < 1$ it is necessary that $\text{sign}(eq_e) = -1$. This means for MBBA with $\text{sign } e = -1$ that the surface charge must be positive. In this

situation, however, homeotropic anchoring of PCB (sign $e = 1$) will be absolutely stable. This roughly corresponds to the experimental finding of much lower tilt for cyanobiphenyl [16]. Taking the experimental value $(n_{cr}/n_m) = 0.625$ we could calculate from (26) with $W_0 = 10^{-3} \text{ J m}^{-2}$ (strong anchoring) $\beta = 8.3 \times 10^{-4}$, i.e. a very low partial positive charge per lecithin molecule suffices to drive the transition. If we include the ordoelectric term, which becomes more important for higher densities (compact monolayer) then we could predict a tilting transition for 5CB as well above a critical value of ΔS (see below) but the general conclusion that the gradient flexoelectric term will tend to suppress the tilt of 5CB at positive surface charge density remains valid.

3.2. Anchoring on dipolar monolayers with variable thickness

Here we analyse the experimental data of Porte [4] concerning the anchoring transition of MBBA on aliphatic monoamine ($C_nH_{2n+1}NH_2$) monolayers by decreasing chain length (see section 1 and figure 2). We assume a certain number of defects (vacancies, dipolar defects) in a square lattice of head group dipoles. The dipole moment of an amino-group attached to an alkyl chain is 1.5 Debye ($5 \times 10^{-30} \text{ Cm}$) with the positive pole facing the glass [25]. The lattice constant of the dipolar lattice is $d_m = \sqrt{l/n_m}$, where n_m is the maximum number of closely packed monoamines. We have seen that defects in such a lattice are equivalent to oppositely directed dipoles (one for a vacancy, two for an antiparallel dipolar defect). We will assume that these defects of area density n_v are also organized in a square superlattice, then its lattice constant will be $d_v = \sqrt{l/n_v}$. The effective dipoles in the knots of the lattice of defects are directed oppositely to the monamine ones, thus they face the LC with positive poles. Consequently, the homeotropic orientation of MBBA is unfavourable both with respect to gradient flexoelectric and dielectric torque (see figure 3) and it is expected to be destabilized, if the surface dipole field is strong enough. Since the anchoring transition appears to be continuous (figure 5) the stabilizing action of the self-energy related to the ordoelectric polarization has also to be taken into account. With the dipolar field in the knots of the lattice given by

$$E = (2\pi\mu/\varepsilon_{LB}\varepsilon_0d_v^3) \exp(-2\pi z/d_v) \quad (27)$$

where μ is the electrical dipole moment and ε_{LB} the dielectric constant of the LB film, the field at a distance from the head groups equal to the monolayer thickness l can be obtained by substituting $z = l$ in (27). This field is denoted by E_0 . In the following it is very useful to use a linear relationship between chain length l and number n of CH_2 groups [26, 25]:

$$l = 0.1265n(\text{nm}) \quad (28)$$

where we disregard the small additional term related to the end CH_2 group.

We have justified above the treatment of this anchoring transition as a local instability. If the anchoring energy is high only in a region of size ξ around the vacancy, then the rest of the liquid crystal will follow the tilt induced by the field around the anchoring points. Thus, (15), where A and B are given by (11) and (12), will hold *locally*, with $\lambda = d_v/2\pi$, E_0 from (27) at $z = l$, $|W|$ the *local* anchoring energy (favouring homeotropy) and $\Delta S = S_b - S_s$, the *local* increment of order parameter (expected to be negative as $S_s > S_b$) will read

$$\begin{aligned} \cos^2 \theta = \frac{1}{3} - A/2B = \frac{1}{3} - (1/2B)^{\frac{1}{2}} [(|\Delta\varepsilon|/8\pi) [(2\pi)^2\mu^2/(\varepsilon\varepsilon_0)^2d_v^5] e^{4\pi l/d_v} \\ + [e|(1 + \Delta S)2\pi\mu/\varepsilon\varepsilon_0d_v^3] e^{2\pi l/d_v} - |W|]. \end{aligned} \quad (29)$$

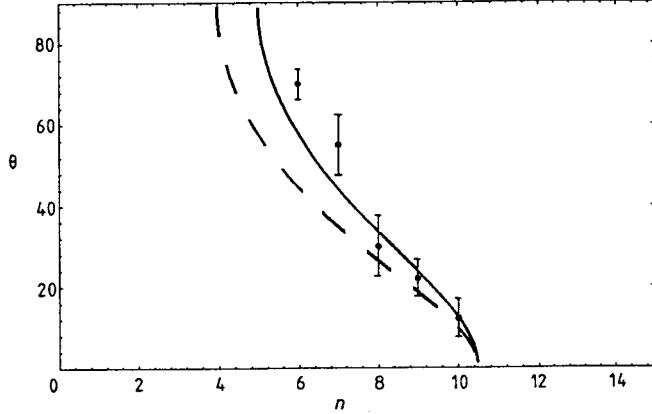


Figure 5. Theoretical fits of tilt angles of MBBA versus aliphatic monoamine chain length [4]. Solid line, $n_s = 5$; dashed lines, $n_s = 4$ (see the text for details).

(29) can be arranged in the form

$$\cos^2 \theta = (1/\alpha)[1 - (\tilde{d}/d_v)^3 \exp(-2\pi l/d_v) - (\tilde{\tilde{d}}/d_v)^5 \exp(-4\pi l/d_v)] \quad (30)$$

where

$$\alpha = 4B/(3|W| - 4B) \quad (31)$$

\tilde{d} is an effective flexoelectric length

$$\tilde{d} = 3\sqrt{2\pi\mu|e|(1 + \Delta S)/\varepsilon_{LB}\varepsilon_0(3|W| + 4B)} \cong 5.1 \text{ nm} \quad (32)$$

and $\tilde{\tilde{d}}$ is an effective dielectric length

$$\tilde{\tilde{d}} = 5\sqrt{|\Delta\varepsilon|\pi\mu^2/2\varepsilon_{LB}^2\varepsilon_0(3|W| + 4B)} \cong 1.3 \text{ nm}. \quad (33)$$

The above mentioned values of \tilde{d} and $\tilde{\tilde{d}}$ were calculated on the basis of material constants of MBBA (see above), of the monoamine film ($\varepsilon_{LB} = 2$, $d_m^2 = 0.2 \text{ nm}^2$, $\mu = 5 \times 10^{-30} \text{ C m}$ [25]), taking also $3|W| + 4B = 2 \times 10^{-4} \text{ J m}^{-2}$ (see table 1). Under these circumstances it can be seen that $(\tilde{\tilde{d}}/d_v)^5$ is almost three orders of magnitude smaller than $(\tilde{d}/d_v)^3$. Having also in mind that the second exponent is a square of the first one, which is less than unity, we could safely neglect the dielectric term in the considerations that follow. In such a case the threshold thickness l_t for tilting instability corresponds to $\cos^2 \theta = 1$, i.e.

$$1 - (\tilde{d}/d_v)^3 \exp(-2\pi l_t/d_v) = \alpha. \quad (34)$$

We can then expand the tilt angle θ around the threshold in terms of a small difference $(l_t - l)$ to obtain

$$\theta^2 = (2\pi/\alpha)(\tilde{d}/d_v)^3(l_t - l)/d_v. \quad (35)$$

Table 1. Parameters of the fits displayed in figure 5 for the two saturation lengths of $n_s = 4$ and $n_s = 5$. d_v is the distance between vacancies; $(d_v/d_m)^2$ is the area per vacancy compared to the area per molecule ($d_m^2 = 0.2 \text{ nm}^2$) or the mean number of molecules with one vacancy; $\alpha = 4B(3|W| + 4B)^{-1}$, from (34); \tilde{d} is the flexoelectric length (36); $(\Delta S)_{1,2}$ are the two roots of (39) (see the text); only the negative root is adopted further on (i.e. $S_s > S_b$); $B = (\Delta S)^2 |e| / 2\epsilon\epsilon_0\xi$, is the ordoelectric parameter ($\xi = 4.45 \text{ nm}$, $e = 2 \times 10^{-11} \text{ C m}^{-1}$); $|W|$ is the local energy of homeotropic anchoring; $|W| = (\frac{2}{3})B(1/\alpha - 1)$. Note that despite the difference in the two fits' parameters, the values for $|W|$ practically coincide.

n_s	$d_v \text{ (nm)}$	$(d_v/d_m)^2$	α	$d \text{ (nm)}$	$(\Delta S)_{1,2}$	$B \text{ (J m}^{-2}\text{)}$	$ W \text{ (J m}^{-2}\text{)}$
4	2.857	41	0.8339	4.13	-0.183	0.225	8.5×10^{-5}
5	3.456	60	0.7152	5.06	-0.133	0.153	4.5×10^{-5}

Thus, we reveal a second-order transition with $\theta \sim \sqrt{l_t - l}$ where decreasing l increases the surface dipoles' field driving the transition. Resorting to the general theory (figure 4) we expect at still shorter chain lengths a second transition to planar state when $\cos^2 \theta = 0$, characterized by a saturation length l_s , which obeys

$$1 - (\tilde{d}/d_v)^3 \exp(-2\pi l_s/d_v) = 0. \quad (36)$$

If we now expand the small difference $\varphi = (\pi/2) - \theta$ around this second transition in terms of $l - l_s$ we obtain

$$\varphi^2 = (2\pi/\alpha)(\tilde{d}/d_v)^3(l - l_s)/d_v. \quad (37)$$

Comparing (35) and (36) we see that the slopes of θ^2 and φ^2 versus Δl are identical. Expressing now l in terms of n via (28) and substituting (34) and (36) in (35) we arrive at an equation for the slope $d\theta^2/dn$ (where d_v has to be expressed in nm):

$$2\pi \exp(2\pi l_s/d_v)[1 - \exp(-2\pi(l_t - l_s)/d_v)]^{-1} 0.1265/d_v = d\theta^2/dn. \quad (38)$$

From (38) the important experimental parameter d_v , the mean distance between vacancies, can be determined.

We plotted the experimental data of Porte [4] for θ^2 (rad) versus chain length and we obtained a very good straight line passing through the first three points ($n = 10, 9, 8$). It intersected the abscissa axis at 10.5 and its slope in (θ^2, n) variables was very close to unity. Thus, the threshold length was determined with a good precision to be

$$l_t = 10.5 \times 0.1265 = 1.33 \text{ nm}.$$

In the vicinity of the second transition only two points were available ($n = 7$ and 6). The slope of the line in variables (φ^2, n) for $n = 7$ and 6 was larger than unity, but this could be expected in view of the uncertainty of conosopic determination of tilt angle in the region of large tilt. This leads to uncertainty in determinating the saturation length $n_s = 5$ or 4.

The transcendent equation (37) for d_v with a slope $d\theta^2/dn = 1$ was solved by MATHEMATICA® software for both $l_s = 0.63 \text{ nm}$ and 0.51 nm . Then \tilde{d} was calculated from (36) and α from (34). The two dependences of θ (°) versus n are shown in figure 5 together with the experimental data of Porte [4]. The parameters of the fit are listed in table 1. One can see that the curve with $n_s = 4$ fits the first three points well, but deviates significantly from the last two. Thus, $n_s = 5$ is more acceptable.

To calculate ΔS , a relationship between \tilde{d} , B and α is obtained from (31) and (32) and then B is expressed in terms of $(\Delta S)^2$ via (13). The resulting quadratic equation reads

$$(\Delta S)^2 - \Sigma(\Delta S + 1) = 0 \quad (39)$$

where

$$\Sigma = \pi \mu \alpha \xi / |e| \tilde{d}^3.$$

The correlation length ξ of the order parameter is calculated according to the Landau–de Gennes theory [27] by

$$\xi = \sqrt{3L_1/a(T_c^* - T)} \quad (40)$$

where $T_c^* = T_c - 1 = 44.6^\circ\text{C}$ in the case of Porte [4], $T_c^* - T \simeq 22\text{ K}$ for T , room temperature, and the other parameters have the following values for MBBA [27]: $L = 6.1 \times 10^{-12}\text{ N}$, $a = 4.2 \times 10^4\text{ J m}^{-3}\text{ K}^{-1}$. This gives $\xi = 4.45\text{ nm}$ for MBBA at room temperature.

From the two roots of (39) the negative ones were chosen to further calculate B and $|W|$ because of the expected enhancing of surface order around the points of anchoring (i.e. the vacancies). The calculated values of $|W|$ are high, but we stress again that these are localized values.

All three important physical parameters d_v , ΔS and $|W|$ characterizing the MBBA–aliphatic monoamine anchoring are obtained from the fit without further assumptions, and there are no free parameters of the fit.

In principle, a hydrophobic surface is capable of inducing a polar ordering i.e. $\langle P_1(\cos\theta) \rangle \neq 0$ of an NLC close to it by means of its biphilic field if the NLC molecules are biphilic dipoles, i.e. if there is a biphilic asymmetry between the end substituents [34, 35]. MBBA is an example of such a biphilic dipole, as argued long ago [36], i.e. a hydrophobic surface interacting preferentially with the butyl tails of MBBA can induce a preferential orientation of the longitudinal electric dipole as well, and, thus, a surface polarization P_s . In a patch of size ξ near a vacancy this polarization will be

$$P_s = \nu \mu_{\parallel} / \xi^2 \quad (41)$$

where μ_{\parallel} is the longitudinal dipole and ν is the number of unipolar ordered molecules in this patch. With $\xi = 4.45\text{ nm}$ as before the total number of LC molecules could not exceed 100. If we take as an upper limit that they are *all* polar oriented, the small longitudinal dipole in the case of MBBA ($\sim 1 \times 10^{-30}\text{ C m}$) could produce surface polarization P_s of $\sim 5 \times 10^{-12}\text{ C m}^{-1}$, which corresponds to our earlier estimates [36].

Now, P_s can couple directly to the surface field of head group dipoles to produce additional surface energy to be added to (11) of the form $P_s E_0 \cos\theta$. This term can stabilize or destabilize the homeotropic orientation depending on the mutual orientation of P_s and E_0 .

If we consider for simplicity a homeotropic anchoring energy term only, from the expression

$$F = \frac{1}{2}|W|(\cos^2\theta - \frac{1}{3}) + P_s E_0 \cos\theta \quad (42)$$

we can find the torque balance equation in the small-angle approximation and we can predict a local instability with a threshold field

$$E_{\text{th}} = |W|/ - P_s \quad (43)$$

where $|W|$ is the local anchoring energy near the vacancy. If we now apply this to the case of Porte's [4] experiment by substituting (27) in (43) we could find a critical thickness for tilt instability:

$$l_{\text{th}} = (d_v/2\pi) \ln(-P_s E_0/3|W|) = (d_v/2\pi) \ln(\nu\mu_{\parallel} 2\pi\mu/3|W_0|\epsilon\epsilon_0 d_v^3 \xi^2). \quad (44)$$

Now, with the values obtained above (table 1) even taking $\nu = 100$ we could see that the term after the logarithm is still below unity (~ 0.6), i.e. with the high value of the local homeotropic anchoring energy and weak longitudinal dipolar moment of MBBA no tilt instability originating from P_s could be observed down to vanishing monolayer thickness l . Additionally, the direction of P_s for MBBA could not be claimed with any degree of certainty, as its longitudinal dipole appears as a small difference of large oppositely directed moments of several dipolar groups. Thus, the dipolar coupling could also be stabilizing the NLC with respect to the instability produced by the quadrupolar coupling, but in the particular case of MBBA-aliphatic monoamine anchoring the stabilizing effect would be negligible, as well.

3.3. Anchoring on multilayer LB films

This anchoring and the transitions observed at a monotonic increase of the number of molecular layers in the film are best discussed in terms of the variations in the geometrical (sterical) roughness and the electrical roughness of the surface. Despite being deposited in compact form, the first molecular layer is likely to contain a large number of defects, being forced to accommodate the geometrical roughness of the substrate. As we have seen, the defects (vacancies, etc) are precursors of homeotropic anchoring. The LB technique in the Y deposition mode is such that the subsequent LB structure, which can be used as an NLC substrate, would have three layers, facing the nematic with the hydrophobic chains of the amphiphiles, then five layers, etc. It is well known that the geometrical roughness of the substrate is screened by such a smectic type of arrangement (see, e.g., [9]). Other substrate properties being successfully screened are van der Waals orienting potentials of anisotropic substrates, and possibly also the electric field of ions on a solid support (glass, etc). Decreasing the number of defects means according to our expression (3) decreasing the strength of homeotropic anchoring. Being left in contact with the electrical roughness of the strongly oscillating dipolar field due to the end groups of the alkyl chains [28–31] on the otherwise molecularly smooth surface of methyl groups, the nematic may well switch to arbitrary orientation due to the reduction of S by the quadrupolar coupling on such a surface (see above), or to a planar anchoring, if the length of longitudinal dipoles of NLC molecules is commensurate with the period of the dipolar field, i.e. $d_m/2$.

In experiments [13] such a switching from homeotropic to tilted orientation of 5CB on behenic acid was observed at five layers. Subsequent experiments with octadecylamine [38] revealed the same critical thickness, the tilt angle this time quickly saturating to 90° at about 15 layers. This may be explained by a lower area per molecule in the latter case, providing better possibilities for locking of the 5CB dipole to the dipolar field.

Recognizing for the first time the importance of the dipolar field of alkyl chains enables us to discuss the difference in the anchoring on saturated fatty acids and unsaturated ω -tricosenoic acid [11]. While the vertical component of the dipole moment of the $-\text{CH}_3$

group is 1×10^{-30} C m with positive pole directed towards the air, the dipole moment of the $-C+H_2=CH_2$ double bond is probably larger and oppositely oriented. Thus, the quadrupolar coupling (e.g. to vacancies) would change its sign. Decreasing the period of the lattice of ω -tricosenoic acid by electron irradiation induced polymerization may bring about an increase of the tilt angle [11] for the same reason as above.

Of course, any discussion of the tilted orientation on LB films should take into account the existence of intrinsic tilt of the LB structure, which may well be thickness dependent [39]. While our discussion was implicitly assumed a normal orientation of the alkyl chains in order to clarify the importance of the gradient surface fields, our next step would be to elaborate upon this further aspect of the steric and van der Waals interaction of the LB film with the NLC, allowing for an internal degree of freedom of tilt in the LB film itself. In this way tilting instabilities of the LB film [19] can enter this already complex but otherwise physically transparent picture.

Some final remarks about the novel concept of electrical roughness deserve mentioning. The strongly disorienting action of a compact alkyl chain surface on an NLC can be a driving force of ordoelectric instability, resulting in a tilt close to the magic angle [13, 32, 33], just like a surface with strong geometrical roughness [37].

From (11) and (16) with $A = -|W_0|/2$ only, the critical value of ΔS can readily be calculated to be

$$\Delta S_{th} = \sqrt{\frac{3}{4}} |W_0| \varepsilon \varepsilon_0 \xi / e^2 \quad (45)$$

which with $|W| = 2.3 \times 10^{-5}$ J m $^{-2}$ (table 1) is $\Delta S_{th} = 0.058$. This is well below the bulk value S_b and thus such a tilt transition is completely feasible, even with anchoring energies higher by an order of magnitude.

Strongly decreased surface order can also explain the observed surface melting under pulsed local heating just a few degrees above room temperature in MBBA [18].

4. Conclusion

By exploring different aspects of geometrical and electrical roughness of LB film treated surfaces and quantifying them in terms of steric, dielectric, gradient flexoelectric and ordoelectric interactions, we proposed in this paper a general theoretical framework for NLC anchoring on LB films. By showing how the non-homogeneous electric fields originating from surface charges and dipoles govern the liquid crystal anchoring by a competition of dielectric, flexoelectric and ordoelectric torques, we predicted a large variety of anchoring states, depending on the sign of surface charges, the orientation of surface dipoles, the signs of dielectric anisotropy and total flexocoefficient and the value of anchoring energy. Anchoring transitions of both first and second order and reentrant sequences, homeotropic–planar–homeotropic and *vice versa*, were also predicted. The theory is compared to the experiment with more than three LB–NLC systems and important parameters of the surface interaction were determined. The model clarified the reason for apparent contradictions between various experiments and put them in a general framework for the first time.

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References

- [1] Proust J E and Ter-Minassian-Saraga L 1972 *C. R. Acad. Sci., Paris* **274** 1105
- [2] Proust J E, Ter-Minassian-Saraga L and Guyon E 1972 *Solid State Commun.* **11** 1227
- [3] Proust J E and Ter-Minassian-Saraga L 1973 *C. R. Acad. Sci., Paris C* **276** 1731
- [4] Porte G 1976 *J. Physique* **37** 1245
- [5] Hiltrop K and Stegemeyer H 1978 *Mol. Cryst. Liq. Cryst. Lett.* **49** 61
- [6] Hiltrop K and Stegemeyer H 1981 *Ber. Bunsenges. Phys. Chem.* **85** 582
- [7] Hiltrop K and Stegemeyer H 1988 *Liquid Crystals and Ordered Fluids* vol 4, ed J Johnson and R Porter (New York: Plenum) p 515
- [8] Hauck G, Komitov L, Derzhanski A and Koswig H D 1982 *Cryst. Res. Technol.* **17** 865
- [9] Blinov L M, Davydova N N, Sonin A A and Yudin S G 1984 *Sov. Phys.-Crystallogr.* **29** 320
- [10] Blinov L M and Sonin A A 1987 *Langmuir* **3** 660
- [11] Saunders F C, Staromlynska J, Smith G W and Daniel M F 1985 *Mol. Cryst. Liq. Cryst.* **122** 297
- [12] Nishikata Y, Morikawa A, Takiguchi Y, Kanemoto A, Kakimoto M and Imai Y 1988 *J. Appl. Phys.* **27** L1163
- [13] Grosperin C 1989 *Rapport de Stage, Laboratoire de Physique des Solides, Orsay*
- [14] Flatischler K, Komitov L, Lagerwall S T, Stebler B and Strigazzi A 1991 *Mol. Cryst. Liq. Cryst.* **198** 119
- [15] Fang J Y, Wei Y, Sun Zh and Stroev P 1991 *Phys. Lett.* **157A** 396
- [16] Fang J, Wei Y and Sun Zh 1992 *Mol. Cryst. Liq. Cryst.* **222** 71
- [17] Komitov L, Stebler B, Gabrielli G, Puggelli M, Sparavigna A and Strigazzi A *Mol. Cryst. Liq. Cryst.* at press
- [18] Shonova N, Petkova J I and Petrov A G *C. R. Acad. Bulg. Sci.* at press
- [19] Alexe-Ionescu A L, Barbero G, Ignatov A and Miraldi E 1992 *Eur. Conf. on Liquid Crystals (Films, 1992)*; 1993 *Appl. Phys. A* **56** 453
- [20] Dubois-Violette E and de Gennes P G 1975 *J. Phys. Lett.* **36** 6255
- [21] Creagh L and Kmetz A 1973 *Mol. Cryst. Liq. Cryst.* **27** 59
- [22] Derzhanski A, Petrov A G, Hinov H P and Markovski B L 1974 *Bulg. J. Phys.* **1** 165
- [23] Prost J and Pershan P S 1976 *J. Appl. Phys.* **47** 2298
- [24] Durand G 1984 *Mol. Cryst. Liq. Cryst.* **113** 236
- [25] Israelachvili J 1992 *Intermolecular and Surface Forces* (London: Academic)
- [26] Tomford C 1980 *The Hydrophobic Effect* (New York: Wiley)
- [27] Priestley E B, Wojtowicz P J and Sheng P (ed) 1979 *Introduction to Liquid Crystals* (New York: Plenum) p 168
- [28] Vogel V and Möbius D 1988 *Thin Solid Films* **159** 73
- [29] Vogel V and Möbius D 1988 *J. Colloid. Interface Sci.* **126** 408
- [30] Beitinger H, Vogel V, Möbius D and Rahman H 1989 *Biochim. Biophys. Acta* **984** 293
- [31] Möbius D, Cordroch W, Loschek R, Chi L F, Dhathathreya A and Vogel V 1989 *Thin Solid Films* **178** 53
- [32] Barbero G, Dozov I, Paliarne J F and Durand G 1986 *Phys. Rev. Lett.* **56** 19
- [33] Durand G 1990 *Physica A* **163** 94
- [34] Derzhanski A and Petrov A G 1982 *Mol. Cryst. Liq. Cryst.* **89** 339
- [35] Petrov A G and Derzhanski A 1987 *Mol. Cryst. Liq. Cryst. Lett.* **151** 303
- [36] Petrov A G and Derzhanski A 1987 *Mol. Cryst. Liq. Cryst. Lett.* **41** 41
- [37] Monkade M, Boix M and Durand G 1988 *Europhys. Lett.* **5** 697
- [38] Bartolino R, Germain P and Durand G unpublished
- [39] Germain P unpublished