Anchoring transitions with polar and non-polar nematic liquid crystals on incompletely oxidized silane substrates

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Abstract. The active oxygen gas arising from a plasma reactor is used to realize progressive chemical modifications onto silane coatings that could be particularly interesting as alignment layers for liquid crystal display applications. Depending on the oxygen density grafted onto the substrate, these alignment layers provide different zenithal anchoring angles, or pretilt angles, with anchoring transitions, for polar and non-polar nematic liquid crystals as 5CB and MBBA, respectively. The anchoring transitions are found to be smoother with the polar nematics. Such a behavior is discussed in terms of the differential wetting model by adding a cosine term to the interaction energy between the nematic and the substrate. A local justification is proposed for this symmetry breaking term.

PACS. 61.30.Gd Orientational order of liquid crystals; electric and magnetic field effects on order – 64.70.Md Transitions in liquid crystals – 68.45.-v Solid fluid interfaces

1 Introduction

Mostly because of their potential applications, the anchoring properties of the nematic liquid crystals have been intensively investigated during the recent years [1,2]. They result from different physical phenomena. Schematically, the polar or zenithal anchoring angle of the nematic director at the interface is essentially determined from the differential wetting properties of the substrate relative to the two parts of the liquid crystal (LC) molecules, the aliphatic chains and the aromatic cores [3]. On the other hand, the azimuthal anchoring angle arises from the surface anisotropy of the substrate, and more specifically, from its geometric roughness down to the molecular scale [4], or from the orientational ordering of its molecules, as obtained when rubbing polymers [5]. Thus, in order to promote the desired zenithal angle, the substrate surfaces are generally coated with aligning agents, such as amphiphilic molecules or polymers. In this way, it is easy to get homeotropic or planar anchorings. The intermediate anchoring angles between 0° and 90°, are more difficult to obtain. Classically, they are realized with SiO evaporations [4], but recently, a new method has been proposed to this aim, based on the gradual oxidation of organic substrates with active oxygen arising from plasma gas [3]. Here, we report on the anchoring behavior of different nematics onto substrates obtained in this manner. We discuss our experimental results according to the dipolar and non-dipolar nature of the nematic molecules, and we extend the differential wetting model of the non-dipolar nematics to the dipolar case.

2 Experiments
2.1 Surface treatments

In this new anchoring treatment, the glass plates are first rubbed at a submicrometer scale with alumina powder and carefully coated with n-octadecyl tri-chlorosilane (OTS) according to standard methods [6]. Then, the silane covering is oxidized with active gas arising from a plasma reactor working with oxygen (86%) and nitrogen (14%) gas at a pressure of 2.5 torr. The plasma contains many different ions that recombine quickly, so that at a distance $d \sim 20$ cm from the source where the sample plates are placed, they are completely annihilated. The gas there, is essentially composed of the original molecules O_2 and N_2, but it contains also a small quantity of NO_2 and of atomic oxygen O. This atomic oxygen is the main chemical agent of the silane oxidation. Without adding the small amount of nitrogen, the atomic oxygen is produced in so large a quantity in the plasma reactor, and is so active too, that the silane substrates are immediately burnt out in CO_2 and H_2O gas. Here, due to the presence of nitrogen, which combines easily with atomic oxygen, the atomic oxygen concentration in the output gas is strongly reduced down, so that the oxidation of the silanized substrates keeps incomplete even after exposure times several minutes long.

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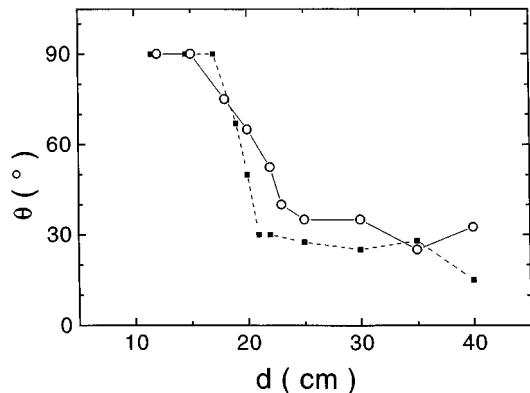[b] *Present address*: Politecnico di Torino, Corso D. degli Abruzzi 24, 10129 Torino, Italy.

Fig. 1. Zenithal anchoring angles θ measured from the normal to the substrate, as a function of the oxidation distance d from the plasma source, respectively, with MBBA (closed squares) and 5CB (open circles), at $22\,°C$. The exposure time to the atomic oxygen gas is 2.5 min. The broken and solid lines are only guides for the eyes. Except in the quasi-homeotropic region, the experimental errors essentially arise from the control of the plasma energy in spite of the stabilization realized by means of fluorescence. Converted in the d scale, the errors may be estimated to amount to about one centimeter.

As shown by means of XPS-analyses, different chemical functions exhibiting a strong permanent dipole moment (alcohol, ketone, aldehyde, acid, ...) are grafted in this manner onto the plates, with a concentration decreasing roughly exponentially as a function of the distance d from the plasma reactor, the characteristic distance being a few centimeters long. Moreover, due to the contact of nitrogen with the atomic oxygen gas, NO_2 molecules are produced in an excited state that further deactivates emitting fluorescence light between 400 and 700 nm. The observation of this fluorescence thus yields an indirect signature to the presence of atomic oxygen. We measure its intensity with a phototransistor, and use it as a guide to tune the microwave excitation of the plasma and thereby to keep the atomic oxygen concentration at a constant level.

2.2 Tilt angle determination

The treated plates are then assembled with parallel rubbing directions to build up cells of thickness $e \sim 5\,\mu m$ as described in reference [7]. No particular attention has been paid on the parallel or antiparallel manner that the cells are assembled since all the treatments performed for the surface preparation, are symmetric, except the unidirectional polishing of the glass plates with the alumina powder which seems not to depend on the rubbing sense. Then, the cells are filled with n-(methoxybenziliden)-butylanilin (MBBA) or with pentyl-cyano-biphenyl (5CB). Both liquid crystals are in the nematic phase at room temperature, but they are introduced in the isotropic phase, well above the nematic transition to avoid the parasitic orientational effects produced by the shear flow in the nematic phase. In this manner, the samples exhibit a uniform orientation in the nematic phase at $22\,°C$, except for some defect lines. As the tilt angle measurements show, these defect lines are in fact disclination walls where the nematic orientation is

reversed. Each time that the isotropic to nematic transition is crossed over, the patterns drawn by the walls, are changed. This indicates that the sample orientation is not related to the filling procedure, and that both signs of the anchoring tilt angle on the substrate are equally possible. Aside to the walls, wide uniformly oriented areas may be used to determine the optical birefringence of the samples, and to deduce their average bulk orientation. Optical interferences are performed to this aim between the ordinary and extraordinary rays, at normal and tilted incidences, according to a method equivalent to classical conoscopy restricted to particular angles [7]. The treatments being identical on both the cell plates, the anchoring angles should be the same. Two symmetric orientations of the nematic may arise inside the cell. One of them is strongly distorted. The other one is uniform if one disregards the orientational distortions due to K_{13} effects, and localized at a molecular distance from the substrate [8]. The average tilt angle, optically measured in such cells, therefore yields the macroscopic anchoring angle onto the treated plates.

2.3 Experimental results

In Figure 1, are shown the zenithal anchoring angles θ measured for MBBA (closed squares) and 5CB (open dots), as functions of the distance d of the silanized plates from the plasma reactor during oxidation. In both cases, an anchoring transition is observed with intermediate anchoring angles between the planar and the quasi-homeotropic orientations. The anchoring angle onto the silanized plates before oxidation is found to range from $20°$ to $30°$. Such a quasi-homeotropic orientation is surprizing since silane substrates are usually known to yield perfect homeotropic anchorings with an anchoring angle $\theta = 0°$. Though the simplest explanation for this observation could be that our silanization process is not clean enough, we cannot discard that the silanization process is more or less always imperfectly realized, leaving numerous untreated holes at the surface of the substrate, even when working in the most careful manner. This point has recently been confirmed with AFM observations [9]. In unrubbed samples, a small tilt angle should then occur randomly in every azimuthal directions. However, because of the elastic interactions, the director cannot follow a too versatile statistics; it would then generally prefer to orient along the average direction, perpendicular to the plates, leading to the observed homeotropic anchoring.

3 Discussion

Essentially, the anchoring transition may be explained in terms of molecular interactions and differential wetting [3]. Because the van der Waals interactions favor the contact of resembling chemical functions, the aliphatic chains of the LC molecules prefer to get closer than the cores to the weakly oxidized silane surfaces, as realized in our setup at large distances d from the plasma source. In this way, one obtains homeotropic or quasi-homeotropic anchorings. On the opposite, when the oxidation has been more active, at

smaller distances d or with longer exposure times, numerous chemical functions with strong dipole moments, *e.g.* alcohol, ketone, aldehyde, acid, ... are synthesized onto the silane plates. The substrate thus contains more polarizable electrons and dipolar moments, and attracts the cores of the molecules preferentially to the aliphatic chains, leading to planar anchorings.

3.1 Non-polar free energy

More quantitatively, such a behavior with anchoring angles depending on the substrate oxidation means that the interaction energy of the LC molecules with the substrate, is a function of the angle θ that they make with the normal to the substrate, and of N, the surface density of the oxygens implanted onto the substrate. Let us analyze in which manner. If the molecules, like MBBA, have a negligible longitudinal dipole moment, the two orientations θ and $\pi - \theta$ are equivalent. To the lowest order in $\cos\theta$ and $\sin\theta$, the interaction free energy, expressed per surface unit of the substrate, may then be expended as [10]:

$$f = f_2 \cos^2 \theta. \qquad (1)$$

In order to discuss the f_2 dependence on N, the oxygen concentration at the substrate interface, let us now detail the different molecular interactions which enter into f. When the LC molecules, as the MBBA and 5CB molecules used here, do not develop hydrogen boundings, the above macroscopic expression is essentially relevant to the Keesom and London (KL) interactions, and mainly to their isotropic contributions [11]. As discussed above and estimated from equation (5) in reference [3] using the Fowkes and Girifalco's theory [12], this KL isotropic contribution may be expressed in terms of the wetting energy difference of the substrate relative to the cores of the LC molecules and to their aliphatic chains. To a first order approximation, the differential wetting energy is thus proportional to the number of the polar centers at the surface, able to produce excess KL interactions, *i.e.* is linear in N.

Apart from this major isotropic contribution, the KL interactions also yield a direct orientational coupling of the LC molecules with the substrate. This coupling term originates from the dipole moments, permanent and fluctuating, at the surface of the substrate, which locally produce an average normal electric field $\mathbf{E}$ (insert of Fig. 2). The electric field then induces a dipole moment proportional to $E \cos\theta$ onto the LC molecules in the immediate vicinity of the dipole centers. This results in an interaction energy $\sim -\frac{1}{2}\varepsilon_a E^2 \cos^2\theta$ per dipole center on the substrate. In the case that the dipoles onto the substrate are permanent, the polarization in the nematic phase is essentially induced *via* re-orientations of the dipolar LC molecules themselves, in the linear regime of the Boltzmann statistics. This mechanism corresponds to the anisotropic Keesom interaction. At small concentrations of the dipole centers N, the volumes where the dipole centers produce the electric field, are well separated from one another and no interferences can occur between them to modify E significantly. In this case, the number of LC molecules submitted to the permanent electric field $\mathbf{E}$ just increases with
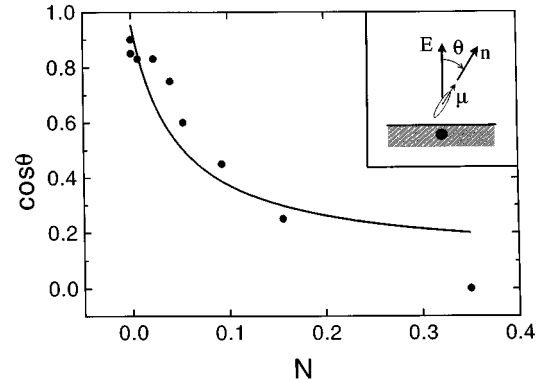

Fig. 2. Cosine of the anchoring angle θ for 5CB at $22\,^\circ$C, as a function of the oxygen density N, determined in arbitrary units from XPS analyses of the oxygen to carbon ratio at the surface. The experimental errors are essentially in the N scale, and roughly amount to $\delta N \sim 0.02$. The solid line is a three-parameters least squares fit of the function, see text, which minimizes equation (3). Insert: Sketch of a dipole center (closed circle) close to the surface of the substrate. It produces an electric field $\mathbf{E}$, normal to the surface in the average. For strong enough $\mathbf{E}$, the orientational statistics of the dipole moment $\boldsymbol{\mu}$ in the neighboring liquid crystal molecules, becomes non-linear and almost saturates. This mechanism leads to a new $\cos\theta$ term in the anchoring energy between the nematic and the substrate.

the concentration of the polar centers onto the substrate, and so, their anisotropic Keesom interaction increases proportionally to N also. At the opposite, for strong oxidations and large N values, the number of LC molecules submitted to the anisotropic Keesom interaction, would stabilize due to the destructive interferences which arise from neighboring dipole centers on the substrate. In order to understand better this effect, one may notice, as is clear from elementary electrostatics, that in the unrealistic limit of a continuous and uniform covering of the surface, the dipoles would generate an electric field $\mathbf{E}$ in the LC medium, which compensates back to zero. Conversely, such destructive interferences cannot occur with the fluctuating dipoles involved in the London interaction, because they are essentially incoherent. The corresponding contribution to the f_2 term, *i.e.* the anisotropic London coupling, is then directly proportional to the number of electronic centers onto the substrate according to their respective polarizability whatever the magnitude of N. So, to the first order approximation in N, both the anisotropic Keesom and London interactions lead to linear behaviors in N, as the differential wetting term.

Adding the three interaction terms, we may thus write $f_2 = A(N - N_0)$ where, the ε_a contribution being secondary, A is essentially determined from the dominant wetting interaction. On the whole, we have:

$$f = A(N - N_0) \cos^2 \theta. \qquad (2)$$

Clearly, equation (2) leads to oversimplified conclusions with two well-cut regimes. It predicts a perfectly homeotropic anchoring, $\theta = 0$, if the oxidation density

N is below the threshold value N_0, and a planar anchoring with $\theta = \pi/2$, at the opposite, for N larger than N_0. In this model, the anchoring transitions are found sharp, and that roughly corresponds to what is observed with a molecule which possesses almost no longitudinal dipolar moment as MBBA (Fig. 1).

3.2 Polar $\cos\theta$-term

The situation is more complicated with molecules, as 5CB which exhibits a strong longitudinal dipolar moment $\mu \sim 4.2$ Debyes essentially localized on the cyano terminal group. The 5CB molecules are largely dimerized in the bulk LC material, with their cyano groups stuck to each other in an antiparallel manner to minimize the electrostatic dipolar energy. However, close to polar surfaces, a lot of the dimers break allowing for monomers to interact electrostatically with the polar centers attached to the substrate. Their interaction energy is all the more important than the dipole moment, tiny at the end of the 5CB molecule, is able to approach very close to the polar centers. Taking the dipole signs into account, we see that the 5CB molecules will essentially be attracted by dipole moments oriented outwards from the substrate. We may then suspect them to be mostly OH centers grafted at the solid surface, or possibly belonging to H_2O molecules H-bounded to other polar centers of the substrate, as the oxygen of an acid, or of an aldehyde chemical function. This globally results in a dipolar ordering of the LC molecules close to the substrate as moreover evidenced with non-linear optics [13].

More precisely, very close to polar centers, the LC molecules, which in the average have to keep parallel to the director $\mathbf{n}$, undergo an electric field $\mathbf{E}$ strong enough to orient them completely in its sense. Their orientational statistics is then saturated or quasi-saturated, with a probability $p_0 \exp \boldsymbol{\mu}.\mathbf{E}/k_B T \sim 1$. In this case which arises for large μE products compared to $k_B T$, the average interaction energy of the molecules with the substrate is $-\mu E \cos \theta$ [14]. It clearly differs from the small μE case discussed in Section 3.1, where the orientational statistics is linear in $\cos \theta$. As is well-known, a polarization is then induced proportionally to $E \cos \theta$ onto the LC molecules, and their interaction energy with the substrate is $-\frac{1}{2}\varepsilon_a E^2 \cos^2 \theta$. On the other hand, if μE is much larger than $k_B T$, the LC molecules are not only oriented unidirectionally with the coupling energy $-\mu E \cos \theta$. They are moreover stuck onto the polar centers of the substrate. This leads to a second orientation mechanism for the LC molecules, based on the hinge effect considered in reference [13]. However, this second mechanism is restricted to the LC molecules in direct contact to the strongest polar centers, although the first one, the electrostatic coupling with a quasi-saturated orientational statistics, could concern more LC molecules close to dipolar centers of intermediate strength. Considering for instance, the OH dipole moment of 1.5D [11], the condition for a strong orientational effect is fulfilled as long as the CN-group of the LC molecule is within a distance of a few Angstroms from it. This mechanism allows weakly accessible polar centers, a little bit buried into the substrate, to contribute as well to the dipolar ordering of the LC molecules. In some manner, it generalizes the hinge mechanism, proposed in reference [13], which restricts the orientational effect to only one LC molecule per polar center at the very surface of the substrate. Per surface unit, and for small N-densities for the interferences between the neighboring dipole centers be negligible, we thus have to add a new term, $-\mu EN \cos \theta$, to the previous interaction energy (2). As noticed above, in the academic case of a uniform covering of identical dipolar centers onto the substrat, the interferences would cancel E to zero and consequently, the $N \cos \theta$ coupling term would vanish. This remark shows that the local justification of this $N \cos \theta$ term is not so trivial as it could seem at the macroscopic scale on the basis of symmetry arguments.

Letting $p = \mu E$, an essentially positive parameter, the interaction free energy f for a polar nematic with a substrate becomes:

$$f = -pN \cos \theta + A(N - N_0) \cos^2 \theta. \tag{3}$$

Minimizing f, we see that the zenithal anchoring angle θ keeps equal to zero for oxidation densities N smaller than the threshold $N^* = 2AN_0/(2A - p)$, which can be reached only if $p < 2A$; and $\theta = \cos^{-1}\left(\frac{pN}{2A(N - N_0)}\right)$, for N larger than N^*. For simplicity, we only consider the positive sign in this expression, but the other sign is equally possible too, since all the problem, starting from the elementary interactions which enter into f, is completely symmetric referred to the normal to the substrate. As in the non-polar case (Sect. 3.1) but in a smoother manner, the zenithal anchoring angle θ of the polar nematics is thus found to increase with N, until the never reached asymptotic value $\pi/2$. So, in this model, the transition to planar anchorings does not really occur.

3.3 Experimental comparisons

Before performing quantitative comparisons to the experimental results, let us notice that expression (3) is symmetric for both signs of the anchoring tilt, as it should be to be consistent with the observations of tilt reversals in the samples after the LC is melt into the isotropic phase.

Our experimental data on 5CB, $\cos \theta$ *versus* the oxygen density, are shown in Figure 2. The oxygen density N, is plotted in arbitrary units since experimentally it is measured by means of XPS analyses to within a coefficient difficult to determine accurately. As noticed above, the anchoring angles are not found to vanish completely, even without any additional oxidation. This observation may be interpreted in terms of an incomplete silane coating of the substrate. A certain amount of oxygens are already present at the glass surface before plasma action. They play the role of some initial oxidation from the point of view of the LC molecular interactions with the substrate. Such an initial oxidation, of surface density N_i, thus adds up to the oxidation, of surface density N, which is due to the oxygen gas arising from the plasma reactor. N has

therefore to be replaced by $N + N_i$ in the above anchoring angle formulae. In particular, equation (3) becomes:

$$f = -p(N + N_i)\cos\theta + A(N + N_i - N_0)\cos^2\theta. \quad (4)$$

The least squares fitting of the theoretical $\cos\theta$ function, with the supplementary parameter N_i, is depicted as a solid line in Figure 2. It is qualitatively correct, except for the large N's where $\cos\theta$ is observed to quickly decrease to zero. This effect may be due to the interferences between neighboring dipole centers, which lead to a significant reduction of the $\cos\theta$ term in equation (3). The characteristic range of the orientational effects of the OH dipole moments being estimated to be a few Angstroms, see above, we may deduce that the destructive interferences become negligible when the average distance between the dipole moments on the substrate exceeds a few nanometers, *i.e.* for N roughly smaller than 10^{17} m^{-2}. This crossover value could correspond about to $N \sim 0.2$ in our experimental units (Fig. 2).

We now discuss the values of the parameters found in the fit. The result $p/A \sim 0.2$ indicates that the linear term in $\cos\theta$ is smaller than the quadratic one in $\cos^2\theta$. Such an unusual behavior could seem surprising. However, this may be understood rather simply if one remembers that the $\cos^2\theta$ term essentially originates from the differential wetting term (Sect. 3.1) to which all the molecules at the surface contribute, whereas the $\cos\theta$ term is restricted to the less numerous LC molecules close to a polar center. The other fitting parameters are found to worth $N_0 = 0.4$ and $N_i = 0.45$, respectively. This puts the real N^*-threshold close to zero and eventually makes it negative within our uncertainties of measurements. As a consequence, the transition from the homeotropic to the tilted anchoring in the small N region, is not experimentally observed here. Conversely, the second transition from the tilted to the planar anchoring, that one seems to observe around $N = 0.2-0.3$, is not formally described in this simple model. This is a direct consequence of the dipolar term in equation (3) which breaks symmetry around $\cos\theta = 0$, making this point unable to correspond to an equilibrium state. We experimentally observe this transition however, because the term in $\cos\theta$ vanishes at large N, as a consequence of the destructive interferences between the dipole centers when they are close enough to one another.

Let us emphasize that the above expressions (2, 3) arise from a first order calculation. The coefficient f_2, which is of relatively large amplitude, should better be expanded up to the N^2 term. With this additional term, the anchoring transitions would become continuous instead of exhibiting sharp jumps as given from equation (2). Clearly, such a smoother behavior is consistent with the transitions observed in non-dipolar LC molecules as MBBA. Let us incidentally notice that the N^2 term has indeed already been introduced to describe the anchoring transitions in MBBA, but in an indirect manner through the more complete Fowkes–Girifalco's description of reference [3]. This N_2 term would naturally exist also in the case of dipolar LC molecules, broadening a little bit more the anchoring transitions. For the moment, our experimental data are not accurate enough to support a fourth fitting parameter, and to allow us to analyze the anchoring transitions to a higher order expansion.

4 Conclusions

In summary, using plasma gas, we have realized slight and controlled oxidations of silanized substrates. With this process, we are able to continuously tune the wetting properties on glass surfaces, and thus to adjust the zenithal anchoring angle of nematic liquid crystals onto glass substrates rather accurately. Moreover, this action on the zenithal angle may be superimposed without any problem to the unidirectional rubbing performed to define the azimuthal anchoring angle; probably because the deposited silane layer is thin enough not to even up the aligning microgrooves that the rubbing has produced. In this way, we observe an anchoring transition from the quasi-homeotropic to the planar orientation. The transition is found sharper with the non-dipolar molecules (MBBA) than with the polar ones (5CB). Such a behavior may be explained in terms of the differential wetting model, initially designed to the non-dipolar case, but extendible to the dipolar one. In this way, a cosine term not so trivial as it could seem at first sight, since it breaks the quadrupolar symmetry of the nematic phase, is added to the interaction energy.

References

1. J. Cognard, Mol. Cryst. Liq. Cryst. **1**, 1 (1982).
2. B. Jérôme, Rep. Prog. Phys. **54**, 391 (1991).
3. P. Hubert, Y. Galerne, Appl. Phys. Lett. **71**, 1050 (1997).
4. M. Monkade, M. Boix, G. Durand, Europhys. Lett. **5**, 697, (1988).
5. J.M. Geary, J.W. Goodby, A.R. Kmetz, J.S. Patel, J. Appl. Phys. **62**, 4100 (1987).
6. J. Sagiv, J. Am. Chem. Soc. **102**, 92 (1980).
7. P. Hubert, H. Dreyfus, D. Guillon, Y. Galerne, J. Phys. II France **5**, 1371 (1995).
8. G. Barbero, N.V. Madhusudana, C. Oldano, J. Phys. France **50**, 2263 (1989).
9. A. Barrat, P. Silberzan, L. Bourdieu, D. Chatenay, Europhys. Lett. **20**, 633 (1992).
10. A. Rapini, M. Papoular, J. Phys. Colloq. France **30**, C4-54 (1969).
11. J.N. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1985).
12. S. Wu, *Polymer Interface and Adhesion* (Marcel Dekker, New York, 1982).
13. X. Zhuang, D. Wilk, L. Marrucci, Y.R. Shen, Phys. Rev. Lett. **75**, 2144 (1995).
14. The quasi-saturated orientational statistics of the LC molecules close to the dipolar centers has also the indirect consequence to reduce the LC polarisability to other applied electric fields, and therefore to lead to reduced effective dielectric constants for these particular molecules.