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MICROSCOPIC DESCRIPTION OF ANCHORING TRANSITIONS

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Abstract The anchoring direction taken by a nematic liquid crystal at the surface of a substrate can be varied, leading to anchoring transitions. Several examples of such transitions have been observed at the surface of mica when the system is put in presence of water and alcohol vapour. A macroscopic model, characterizing the liquid crystal–mica interface by its energy as a function of the liquid-crystal orientation, can reproduce all the observed transitions but does not give any information about the microscopic mechanisms leading to these transitions. More insight on these mechanisms is obtained from studies of the orientational distribution of the liquid crystal molecules in contact with the substrate performed using optical second-harmonic generation. These studies show that the bulk reorientation characterizing the first-order anchoring transitions observed on mica is driven by a first-order orientational transition in the surface liquid crystalline layer. More generally, these studies provide the boundary conditions on the liquid crystalline orientational order necessary for a microscopic description of the order close to a substrate surface.

INTRODUCTION

Nematic liquid crystals have the property of being easily oriented by surfaces, in particular solid substrates. This phenomenon is called anchoring and refers to the orientation of the director in a given direction with respect to the substrate surface [1]. Anchoring is the result of complexe mechanisms taking place in the vicinity of the surface. Generally speaking, we can distinguish several regions in a liquid crystal in contact with a substrate (Fig. 1a). Far from the substrate, there is the bulk liquid crystal, with all the molecules having the same mean orientation. Right at the surface, the liquid-crystal molecules are in direct interaction with the substrate and have their orientational distribution determined by this interaction. In between, there is a transition region —or interfacial region— in which the molecular order evolves from the one in the surface layer to the one in the bulk. Just outside this region, the director has a given orientation which depends on the structure of the

interfacial region; this orientation is the anchoring direction of the liquid crystral at the surface [1].

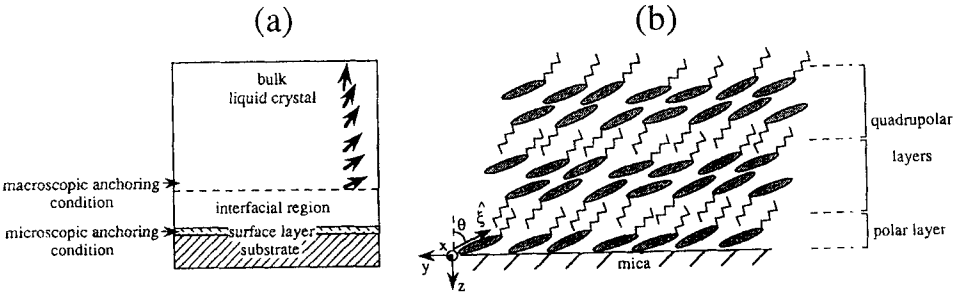

FIGURE 1: (a) Schematic representation of the interface between a nematic liquid crystal and a substrate; (b) organization of the liquid crystal molecules close to the substrate; the liquid crystal molecules are made of a cyanobiphenyl core represented by an ellips and an aliphatic chain represented by a saw-tooth line.

Interestingly anchoring transitions [1, 2], i.e. changes in anchoring directions, can be observed. Several examples of such transitions have been reported at the surface of cleaved mica crystals, when the system is put in the presence of water and alcohol vapour [3, 4]. They are due to the adsorption of these volatile molecules at the mica–liquid crystal interface. In order to understand these transitions, we nedd to consider the properties of the interface between the liquid crystal and mica.

MACROSCOPIC DESCRIPTION

Different types of approachs have been used to describe the phenomenon of anchoring. For many years, anchoring has been described with a macroscopic approach which ignores the presence of the interfacial region existing between the substrate surface and the bulk of the liquid crystal. This is equivalent to assume that the bulk structure of the liquid crystal extends right up to the surface. The interface is then characterized by the dependence of its energy γ on the orientation of the director at the surface. This surface energy is a periodic function of the azimuthal angle ϕ and the tilt angle θ defining the orientation of the director at the surface. Its general

form can then be writen as a development in spherical harmonics $Y_l^m(\theta, \phi)$:

$$\gamma(\theta, \phi) = \sum_{l,m} A_{lm} Y_l^m(\theta, \phi). \quad (1)$$

Using the symmetry of the surface, this development can by simplified by suppressing all the terms which are not invariant by this symmetry. Minimizing this surface energy leads to the anchoring diagram giving the anchoring directions induced by the surface as a function of the coefficients A_{lm} appearing in the development of γ.

Knowing that the mica surface has a mirror symmetry [5] and orients the liquid crystal parallel to the surface, the dependence of γ on the azimuthal angle ϕ can be written to the lowest three orders as:

$$\gamma(\phi) = a_2 \cos(2\phi) + a_4 \cos(4\phi) + a_6 \cos(6\phi), \quad (2)$$

ϕ being measured from the mirror plane of the mica surface [6].

The anchoring diagram obtained with this form of γ exhibits qualitatively all the features of the experimentally obtained anchoring diagrams, with in particular all the possible anchoring transitions. However this macroscopic description does not give us any information about the mechanisms at the origin of these transitions. In order to understand these mechanisms, we need to consider the behaviour of the interfacial region which exists close to the substrate surface.

MICROSCOPIC DESCRIPTION

The true boundary condition imposed on the distribution of molecular orientations is governed by the interaction potential of the surface molecules with the substrate. The description of anchoring can then be separated into two parts. The first one consists in the determination of the microscopic anchoring conditions on the molecules which interact directly with the substrate. The second part consists in determining how the rest of the liquid crystal adapts itself to these microscopic anchoring conditions via the interfacial region. The way this adaptation occurs depends on the properties of the liquid crystal and determines the macroscopic anchoring condition on the bulk director.

Experimental determination of microscopic anchoring conditions

In practice, instead of the interaction potential of the liquid crystal molecules with the substrate, we can use as alternative microscopic anchoring condition the orientational distribution taken by the surface molecules. This procedure has the great advantage that this distribution is accessible experimentally by means of optical second-harmonic generation [7]. When a surface monolayer of liquid crystal molecules exhibiting a polar ordering (Fig. 1b) is sandwiched between two centro-symmetric media (the substrate and the rest of the liquid crystal) in which the electric-dipole contribution to the second-harmonic generation is forbidden, this layer is mainly responsible for the output second-harmonic signal. This signal can be measured as a function of the sample rotation Φ about its surface normal for different input and output polarization combinations. Fitting the measured data with theory [8] then allows one to determine the nonlinear susceptibility tensor $\bar{\chi}^{(2)}$ of the monolayer. Measurement of $\bar{\chi}^{(2)}$ provides information about the orientational distribution $f(\theta, \phi)$ of the molecules in the monolayer.

Second-harmonic generation has been used to study a first-order transition occurring at the interface between muscovite mica and 4-*n*-pentyloxy-4'-cyanobiphenyl (5OCB) in the presence of ethylene glycol ($HOCH_2CH_2OH$) vapour [9]. Observations with a polarizing microscope of a macroscopic film of 5OCB on muscovite mica had shown that as the partial pressure in ethylene glycol increases, there is a critical value p_c of this pressure at which the bulk of the liquid crystal exhibits a reorientation from a direction perpendicular to the mirror plane of the mica surface to a direction parallel to this plane and to the substrate surface [4].

Second-harmonic generation measurements show that when the partial pressure of ethylene glycol increases from zero, continuous changes in the surface orientational distribution of 5OCB molecules are observed until p_c is reached, at which point a discontinuous variation occurs. The orientational distributions obtained just before and after this first-order transition are given in Fig. 2. These distributions exhibit four peaks. One is close to $\theta = 180$ deg, which corresponds to molecules being perpendicular to the substrate surface pointing with their cyanogroup away from it.

The other peaks correspond to molecules tilted with respect to the substrate surface and pointing with their cyanogroup towards it [10]; one of these peaks is along the surface mirror plane σ and the other two (of which only one appears on the plots of Fig. 2) are symmetric with respect to it. At the transition, the two symmetric peaks of the distribution jump towards the surface mirror plane σ and are depleted in favour of the peak belonging to σ.

Combining the bulk and surface observations leads to the conclusion that the surface transition observed with second-harmonic generation measurements drives the bulk first-order anchoring transition. In order to reinforce this conclusion, we need to reproduce the experimentally observed bulk orientation before and after the anchoring transition using the measured surface orientational distributions as boundary conditions for the orientational order of the liquid crystal.

Theoretical calculation of bulk orientation

A simple way of deducing the bulk orientation from the surface orientational order is to calculate the effective potential of interaction of a bulk molecule with the surface layer, using a simple interaction potential between two molecules. The minimum of this effective potential corresponds to the orientation taken by the bulk. This method predicts correctly the azimuthal orientation of the bulk director but not always its tilt with respect to the surface. In the case of the anchoring transition considered above, it predicts the bulk azimuthal reorientation but after the transition the director is found to be tilted with respect to the surface, which disagrees with the experimental observations [9]. The main defect of this simple model is that it considers the bulk liquid crystal to be in direct contact with the surface layer ignoring the presence of the interfacial region. It basically assumes that the bulk takes the mean orientation of the surface molecules, which obviously is not always true.

In order to consider the variation of the molecular order in the interfacial region, we can describe the orientational order at a given point by the nematic order parameter tensor, whose spatial variation is given by the Landau-de Gennes formalism [11]. This formalism has recently been used to describe several aspects of anchoring [12]-[14].

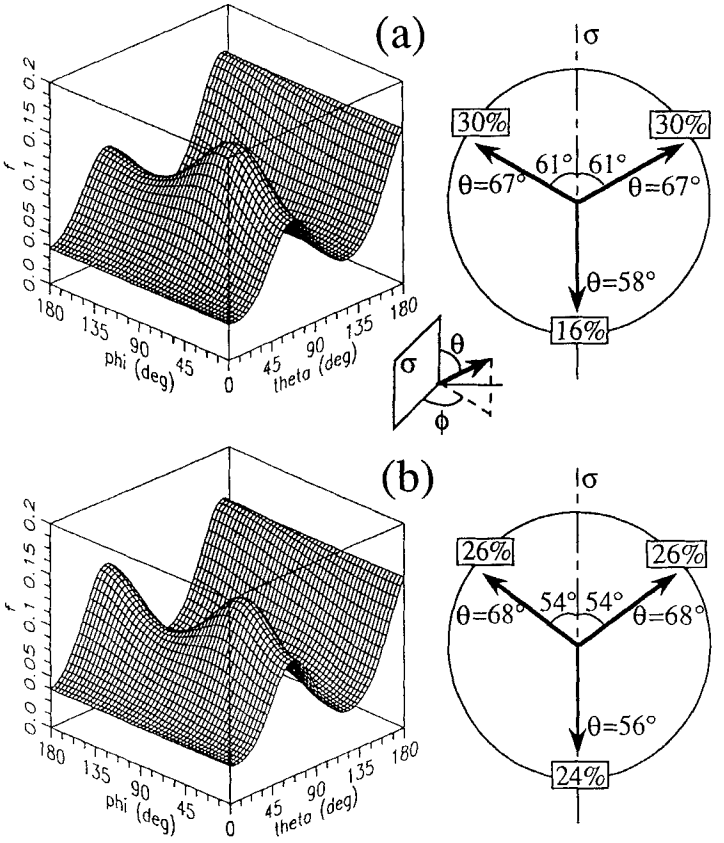

FIGURE 2: Left: orientational distributions $f(\theta, \phi)$ obtained for a 5OCB monolayer on muscovite mica in an atmosphere containing ethylene glycol vapour (a) before the orientational transition and (b) after this transition. θ and ϕ are the spherical coordinates defining the orientation of one molecule; $\phi = 0$ or 180 deg refers to the mirror plane σ of the surface (see inset). For clarity, $f(\theta, \phi)$ is plotted only for $\phi \in [0 \text{ deg}, 180 \text{ deg}]$. Right: position of the different peaks (excluding the one at $\theta \simeq 180$ deg) represented by the arrows and defined by their θ and ϕ coordinates, and proportion of molecules in each of them indicated in the box at the end of each arrow; the plane of the figure corresponds to the substrate surface.

In order to use this formalism in combination with second-harmonic generation measurements [14], we first need to determine the surface value of the order parameter tensor $Q^s_{ij} = \langle 3\xi_i\xi_j - \delta_{ij}\rangle/2$ using the experiementally determined surface orientational distribution $f(\hat{\boldsymbol{\xi}})$. This tensor can be diagonalized in a reference frame having as first axis the mean orientation of the surface molecules represented by the surface director $\boldsymbol{n}_s$:

$$\bar{\boldsymbol{Q}}^s = \begin{pmatrix} Q^s & 0 & 0 \\ 0 & (-Q^s + P^s)/2 & 0 \\ 0 & 0 & (-Q^s - P^s)/2 \end{pmatrix} \tag{3}$$

The coefficient Q^s is the scalar order parameter which indicates how well the molecules are aligned along the director.

In the case of a mica surface, the reference frame in which $\bar{\boldsymbol{Q}}^s$ is diagonal has always one of its axes perpendicular to the surface mirror plane (inset in Fig. 3). In the system before the anchoring transition (Fig. 2a), the surface director is parallel to this particular axis; after the transition (Fig. 2b), it is parallel to one of the axes belonging to the mirror plane, making an angle $\alpha_s = 48\,\text{deg}$ with respect to the surface normal. The surface scalar order parameter Q^s is respectively 0.009 and 0.005; P^s equals 0.02 and 0.005.

Once we have the boundary conditions on the order parameter tensor $\bar{\boldsymbol{Q}}$, we can determine how this tensor evolves as a function of the distance z to the surface by minimizing the Landau-de Gennes free energy of the interface $F = \int \mathrm{d}V(f_u + f_g)$ where:

$$\begin{aligned} f_u &= \frac{A_Q}{2}(Q - Q^b)^2 + \frac{A_P}{2}P^2 \\ f_g &= \frac{L_1}{2}\frac{\partial Q_{ij}}{\partial z}\frac{\partial Q_{ij}}{\partial z} + \frac{L_2}{2}\frac{\partial Q_{iz}}{\partial z}\frac{\partial Q_{iz}}{\partial z} \end{aligned} \tag{4}$$

with $Q^b \approx 0.6$ [15] being the bulk value of the scalar order parameter (summation over repeated indices is assumed). For an interface exhibiting a mirror plane and neglecting biaxiality ($P = 0$), f_g becomes:

$$f_g = \frac{1}{4}\left[\left(3L_1 + \frac{5}{4}L_2\right) + \frac{3}{4}L_2\cos 2\alpha\right]\left(\frac{\partial Q}{\partial z}\right)^2 + \frac{9}{4}\left(L_1 + \frac{1}{2}L_2\right)\left(\frac{\partial \alpha}{\partial z}\right)^2 Q^2$$

$$-\frac{3}{8}L_2 \sin 2\alpha \frac{\partial \alpha}{\partial z} Q \frac{\partial Q}{\partial z} \tag{5}$$

where α is the angle between the director and the z-axis perpendicular to the surface (inset of Fig. 3). The last term couples the gradients of Q and α and favours configurations in which these gradients have the same sign. On mica, Q is lower at the surface than in the bulk, so that both Q and α increase as one moves away from the surface.

Before the anchoring transition, the director does not vary spatially and remains perpendicular to the mirror plane, which is the experimentally observed bulk orientation. After the transition, the director evolves towards the surface plane as one moves away from the surface. Numerically solving the Euler-Lagrange equations obtained from equations (2) and (3) for $A_Q/L_2 = 0.01$ nm^{-2} and $L_1/L_2 = 2/5$ [15, 16] gives the profile of Q and α in the interfacial region (Fig. 3). The bulk value of the angle α is found to be 87.7 deg, which corresponds to a bulk director close to the one observed experimentally for which $\alpha = 90$ deg. The decay length $\xi_Q \approx 10$ nm of Q is the thickness of the interfacial region and is equal to the coherence length $\xi \approx (L_2/A_Q)^{0.5}$ of the nematic order [17]. The decay length of α is very short (≈ 1 nm). This is due to the fact that variations in α are less unfavourable where the liquid crystal is little ordered (see the second term of equation (5)), which happens close to the surface.

CONCLUSION

From the results presented here, we can draw several conclusions. The first one concerns the anchoring transitions observed on mica in the presence of ethylene glycol vapour. The second-harmonic generation measurements show that the bulk reorientation characterizing these transitions is driven by an orientational transition taking place in the layer of liquid crystal molecules in contact with mica.

A second conclusion concerns the orientational order of the liquid crystal in the interfacial region. By the direct observation of a large director variation in the interfacial region, we unambiguously confirm the fact that the director can vary in the interfacial region because of a coupling with the degree of orientational order

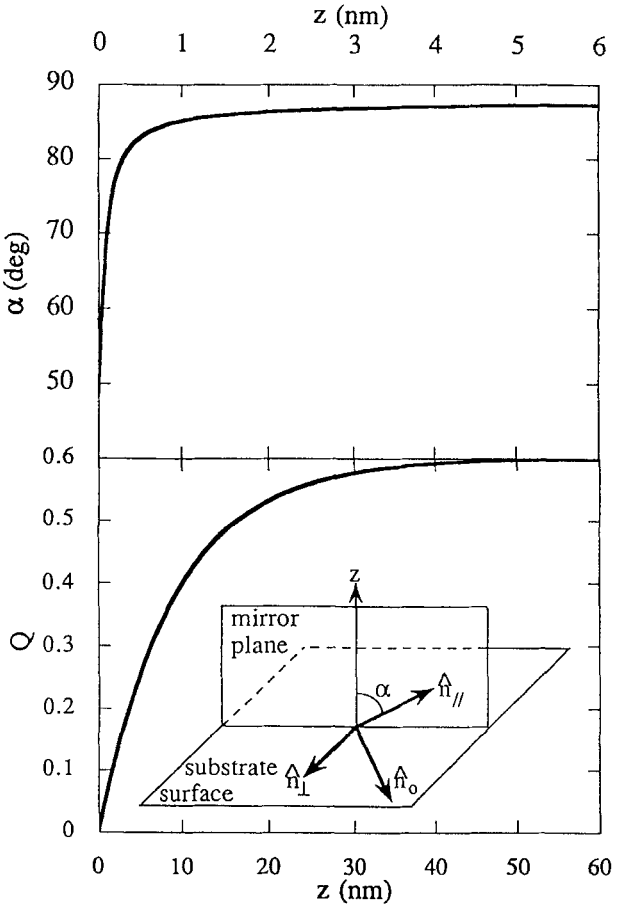

FIGURE 3: Spatial variation of the scalar order parameter Q and the angle α made by the director with the surface normal in a nematic liquid crystal whose surface molecules have the orientational distribution given in Fig. 2b. Inset: reference frame $(\hat{\boldsymbol{n}}_i)$ in which the order parameter tensor $\bar{\boldsymbol{Q}}$ is diagonal. The director respectively coincides with $\hat{\boldsymbol{n}}_\perp$ and $\hat{\boldsymbol{n}}_{||}$ before and after the anchoring transition.

[12, 14]. However this variation can be forbidden by the symmetry of the interface: it can only occur if the interface has no symmetry or if it has a mirror symmetry with the director in the mirror plane.

A last conclusion concerns anchoring on flat surfaces in general. We have seen that the Landau-de Gennes formalism allows to predict within a few degrees the bulk orientation of the liquid crystal starting from the surface orientational order. This means that the bulk orientation is not sensitive to the details of the surface orientational distribution but depends essentially on the average nematic-like order described by the order parameter tensor.

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REFERENCES

1. B. Jérôme, Rep. Prog. Phys. **54**, 391 (1991).
2. P. Pieranski and B. Jérôme, Mol. Cryst. Liq. Cryst. **199**, 167 (1991).
3. P. Pieranski and B. Jérôme, Phys. Rev. A **40**, 317 (1989).
4. J. Bechhoefer, J.L. Duvail, L. Masson, B. Jérôme, R.M. Hornreich, and P. Pieranski, Phys. Rev. Lett. **64**, 1911 (1990).
5. Micas, vol. 13 of Reviews of Mineralogy, S.W. Bailey, editor (Brookcrafters, Chelsea, 1987).
6. P. Pieranski, B. Jérôme, and M. Gabay, Mol. Cryst. Liq. Cryst. **179**, 285 (1990); H.S. Kitzerow, B. Jérôme, and P. Pieranski, Physica A **174**, 163 (1991).
7. Y.R. Shen, Nature **337**, 519 (1989).
8. M.B. Feller, W. Chen, and Y.R. Shen, Phys. Rev. A **43**, 6778 (1991).

9. B. Jérôme, J. O'Brien, Y. Ouchi, C. Stanners, and Y.R. Shen, Phys. Rev. Lett. **71**, 758 (1993); B. Jérôme and Y.R. Shen, Phys. Rev. E (in press).

10. P. Guyot-Sionnest, H. Hsiung, and Y.R. Shen, Phys. Rev. Lett. **57**, 2963 (1986).

11. P.G. de Gennes, Mol. Cryst. Liq. Cryst. **12**, 193 (1971).

12. G. Barbero and G. Durand, J. Appl. Phys. **69**, 6968 (1991); R. Barberi, G. Barbero, and C. Ferrero, Mol. Mat. (in press).

13. P.I.C. Teixeira, T.J. Sluckin, and D.E. Sullivan, Liq. Cryst. **14**, 1243 (1993).

14. D. Johannsmann, H. Zhou, P. Sonderkaer, H. Wierenga, B.O. Myrvold, and Y.R. Shen, Phys. Rev. E **48**, 1889 (1993).

15. N.V. Madhusudana and R. Pratibha, Mol. Cryst. Liq. Cryst. **89**, 249 (1982).

16. G. Vertogen and W.H. de Jeu, Thermotropic Liquid Crystals: Fundamentals, Springer Series in Chemical Physics, vol.45 (Springer, Berlin, 1988).

17. T.W. Stinson and J.D. Litster, Phys. Rev. Lett. **30**, 688 (1973).