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## Nematic Liquid Crystals at Interfaces

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## NEMATIC LIQUID CRYSTALS AT INTERFACES

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**Abstract** Through the example of nematic liquid crystals, which are the kind of crystalline phases in which surface effects have most extensively been studied, the principal aspects of the behaviour of liquid crystals at interfaces are presented. They can be separated in two categories. First, the presence of another phase in contact with the liquid crystal induces a perturbation of the liquid crystalline order. Second, the presence of a surface limiting the liquid crystalline phase has a macroscopic effect on the bulk of the phase : in absence of any other orienting field, the surface can impose the orientation of the whole phase. This orienting effect of surfaces on liquid crystals is the so-called anchoring phenomenon. These two aspects of surface effects are linked to each other as the induced anchoring direction depends on the structure of the perturbed region.

*Keywords:* liquid crystals, solid-fluid interfaces, fluid-fluid interfaces, surface induced order

### I. INTRODUCTION

The first surface effect which has been observed in nematic liquid crystals is the orientation of these phases by solid surfaces, discovered at the beginning of this century by Mauguin<sup>1</sup>. Since then, this macroscopic effect of surfaces on the bulk nematic phase -called *anchoring*- has been extensively studied and a lot of effort has been dedicated to find the microscopic origin of this effect.

When the nematic phase is put in contact with another phase (solid, liquid or gas), a surface is created which limits the nematic phase. In the case the other phase is a solid or a liquid substrate, this surface is simply the surface of the substrate ; in the other cases, the position of this surface can be arbitrarily chosen. The presence of this other phase induces a perturbation of the nematic order over a thickness  $\xi_i$  near the surface (Fig. 1). When the system is far from any phase transition of the bulk, which is the case we consider here,  $\xi_i$  is of the order of a few molecular lengths and defines the thickness of the transition region -or interface- between the nematic phase and the other phase. At a distance of the surface greater than  $\xi_i$ , the nematic order is recovered and the

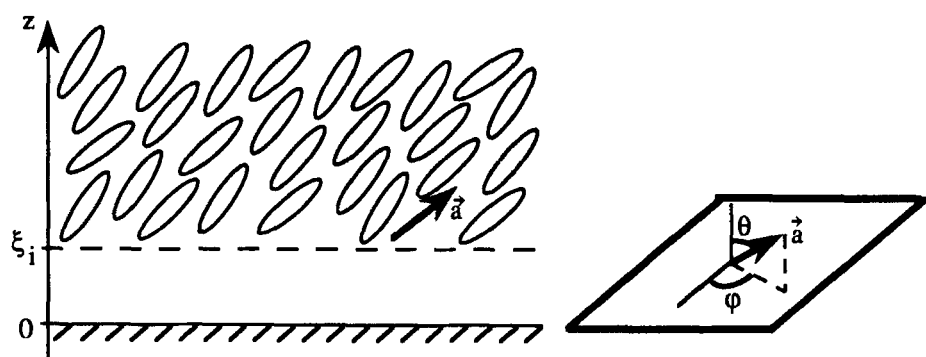


FIGURE 1 Schematic representation of the interface between a nematic liquid crystal and another phase. Inset : azimuthal angle  $\varphi$  and tilt angle  $\theta$  defining an anchoring direction  $\underline{a}$ .

nematic molecules take a fixed mean orientation  $\underline{a}$  which is called the *anchoring direction* of the nematic liquid crystal at the interface. In absence of any other orienting field (electric or magnetic field, flow, other surface...), this orientation is imposed to the molecules of the bulk via the elastic forces which tend to orient all the molecules parallel to each other, leading to the orientation of the nematic phase by the surface.

A convenient concept to describe the anchoring phenomenon is the concept of *anchoring induced by an interface*. The energy of this interface depends among other parameters on the orientation of the molecules in the nematic phase. This energy has a certain number of minima obtained for orientations of the director  $\underline{a}_i$  corresponding to the anchoring directions. The set of anchoring directions  $\{\underline{a}_i\}$  which are possible for a nematic liquid crystal at an interface characterizes the anchoring induced by the interface. This anchoring can be monostable, multistable or degenerate depending on whether the number of elements in the set  $\{\underline{a}_i\}$  is one, a finite number greater than one or infinite. It can also be planar, tilted or homeotropic depending on whether the anchoring directions are parallel, tilted or perpendicular to the plane of the interface.

The main issue concerning anchoring of nematic liquid crystals is to relate the observed anchorings with the structure of the interfaces and to find the microscopic interactions responsible for the orientation of these phases by surfaces. As we will see in Section III, the problem is far from being solved especially with regard to the second point ; even the interface structure is known only in a few systems. We are thus unable to predict from a microscopic basis which anchoring a given interface should induce. This gives some interest

to phenomenological approaches based on a macroscopic point of view.

## II. MACROSCOPIC APPROACH OF ANCHORING

Such approaches consider only the orientation of the nematic phase and the dependence of the interfacial energy  $\gamma_s$  on this orientation, without considering the detailed structure of the interface. The expression of  $\gamma_s$  has then to be found following thermodynamic and symmetry considerations.

### II.1. Prediction of possible anchorings by symmetry arguments

The relevance of symmetry in the problem of anchoring has been first pointed out in the case of crystalline surfaces<sup>2</sup> but symmetry arguments can be used for any surface in order to make some predictions over the anchorings we can expect to observe on such surface. The term "surface" means here the surface of the other phase creating the interface with the nematic phase. The symmetry of this surface, which is the symmetry of  $\gamma_s$ , is independent of the behaviour of the nematic phase once it is in contact with the surface and has chosen one of the possible anchoring directions while the symmetry of the interface depends on the orientation taken by the nematic phase. In the case the other phase is a gas or the isotropic phase, we can still in principle distinguish the surface of the other phase which is isotropic ( $C_{\infty v}$  symmetry), even if such surface is not physical, from the interface with the nematic phase which, in the case the induced anchoring is degenerate, is not isotropic because of the selection of one of the possible anchoring directions by the nematic phase.

Just as in an anisotropic space one can obtain only phases whose structure is compatible with this anisotropy, a surface can induce only anchorings compatible with its symmetry. The set of anchoring directions characterizing each of these compatible anchorings can be generated from one anchoring direction by applying all the symmetry elements of the surface<sup>3,4</sup>. The example of the simple mirror symmetry is given in Figure 2. For a given surface, only one of the anchorings allowed by its symmetry is effectively induced depending on its detailed structure.

Such symmetry arguments also allow to obtain the most general shape of the interfacial energy  $\gamma_s$ .  $\gamma_s$  is a periodic function of the azimuthal angle  $\varphi$  and the tilt angle  $\theta$  (with respect to the surface normal) defining the mean orientation of the molecules in the nematic phase (Fig. 1).  $\gamma_s$  can thus be

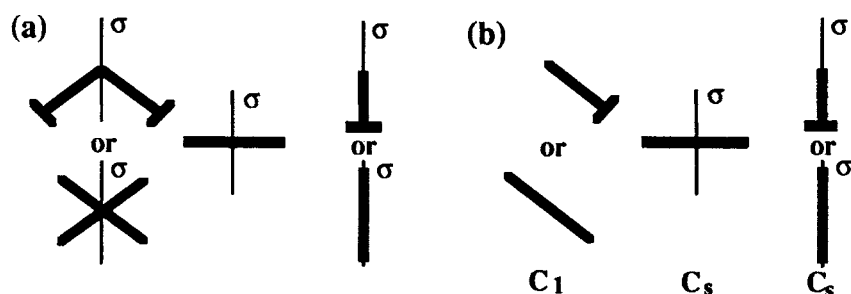


FIGURE 2 (a) Different anchorings which can be found on a surface having a  $C_s$  symmetry characterized by a mirror plane  $\sigma$ ; (b) symmetry of the interface obtained in the case of each anchoring once the nematic liquid crystal has selected one of the possible anchoring directions; this symmetry corresponds to the type of the anchoring. The plane of the figure corresponds to the plane of the surface.

developed in a Fourier series :

$$\gamma_s(\theta, \varphi) = \sum A_{1m} Y_1^m(\theta, \varphi)$$

where  $Y_1^m(\theta, \varphi)$  are spherical harmonics and  $A_{1m}$  are coefficients which are non-zero only if the corresponding  $Y_1^m$  is compatible with the symmetry of the surface. By minimization of  $\gamma_s$ , one can find the anchoring diagram giving the anchorings induced by the surface depending on the values of the coefficients  $A_{1m}$ .

As long as these coefficients are not related to the physical parameters defining the structure of the interface, which would require the knowledge of the mechanisms responsible for anchoring, such anchoring diagram cannot be used to predict which of the anchorings allowed by the symmetry of a surface will be effectively induced by this surface.

## II.2. Anchoring transitions

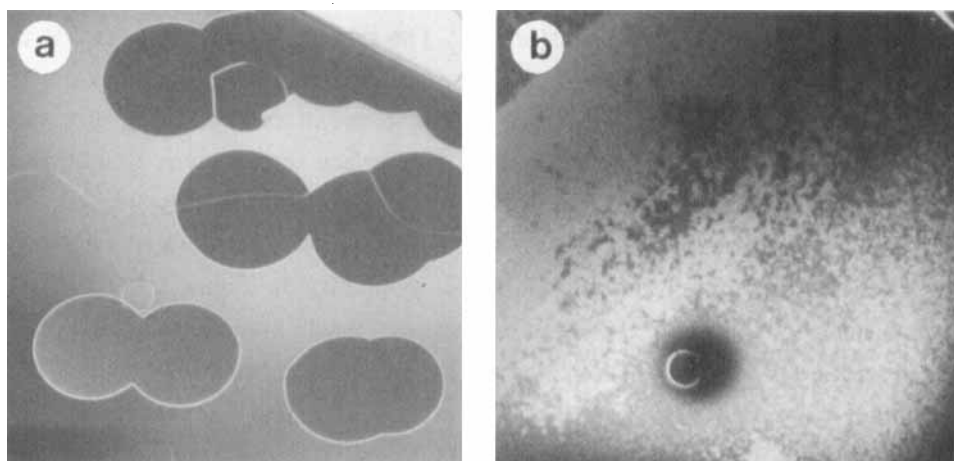
The main interest of these theoretical anchoring diagrams is that they show all the different ways the anchoring can change on surfaces having a given symmetry when some parameters are varied. Such changes, called anchoring transitions, have some common characteristics with phase transitions.

First they follow the same symmetry rules. Second-order anchoring transitions must involve a change of the symmetry of the interface while it is

not the case for first-order transitions<sup>4,5</sup>. The symmetry of the interface is the subgroup of the symmetry group of the surface containing the symmetry elements of the surface which leave invariant one of the anchoring directions characterizing the anchoring induced by the surface. For a given symmetry of the surface, different symmetries of the interface are obtained depending on the orientation of the anchoring directions with respect to the symmetry elements of the surface<sup>4,5</sup> (see the example of  $C_s$  symmetry in Figure 2). Anchoring transitions also appear the same way as phase transitions. First-order transitions (Fig. 3a) are characterized by the nucleation and the growth of domains having a new orientation<sup>6</sup>. Second-order transitions (Fig. 3b) are characterized by the appearance of fluctuations creating domains with very close orientations ; when one moves away from the transition, the orientations separate from each other and the walls between the different domains become more clear<sup>7</sup>.

There are only a few reported examples of experimentally observed anchoring transitions. Most of them are continuous transitions between a conical (tilted degenerate) and a homeotropic anchoring obtained by varying the temperature at the interfaces with carbon-coated glass<sup>8,9</sup>, with air<sup>10,11</sup> and with glass coated with surfactant monolayers<sup>12</sup>. In the last case, the transition could be due to a phase transition occurring in the surfactant monolayer<sup>12</sup>. Another continuous transition driven by temperature has been observed on SiO films evaporated under oblique incidence between a monostable tilted and a bistable tilted anchoring<sup>13</sup>. The last example is a series of transitions driven by the composition in water and alcohol vapours of the atmosphere above the nematic film obtained on the cleavage surfaces of some crystals<sup>5-7,14,15</sup>. Both first- and second-order transitions have been observed between the different planar anchorings induced by gypsum, phlogopite mica and muscovite mica. These transitions are probably due to the dissolution of water and alcohol molecules in the liquid crystal and possibly to the adsorption of these molecules at the substrate surface. Similar transitions have also been obtained by deforming the muscovite mica surface<sup>16</sup>.

The meaning of the term "anchoring transition" can be extended to include transitions between different anchorings obtained on a series of substrates by varying a parameter determining their structure : density of surfactant monolayers<sup>17</sup>, length of aliphatic chains of surfactants<sup>18</sup>, number of surfactant layers in Langmuir-Blodgett films<sup>19</sup>, incidence angle of evaporation of SiO films<sup>20</sup> or thickness of these films<sup>21</sup>. One could also imagine that



**FIGURE 3** Anchoring transitions on muscovite mica driven by the water and ethylene glycol vapour pressures in the atmosphere above the nematic film : (a) first-order transition : domains with a new orientation nucleate and grow (photograph by P. Pieranski) ; (b) second-order transition : fluctuations create domains having very close orientations (photograph by J. Bechhoefer).

See Color Plate I

anchoring transitions could be obtained by changing the molecular structure of the nematogen in a homologous series but no experiment reports any example of such transitions.

The phenomenological approach has been used successfully to reproduce the second-order transitions between homeotropic and conical anchorings<sup>22</sup>, the second-order transitions obtained on SiO films by varying the incidence angle of evaporation<sup>3</sup> and the adsorption-induced and strain-induced transitions obtained on gypsum and mica<sup>5-7,14-16</sup>. In the last case, it is interesting to note that the same expression of  $\gamma_s$  accounts for all the transitions observed on a given substrate whatever the way they are obtained. One has only to change the relationship between the coefficients in the development of  $\gamma_s$  and the physical parameters defining the structure of the interface.

Although quite useful, the predictions of such phenomenological descriptions are somewhat limited. The only way to go beyond phenomenology is to consider the structure of the interface and the mechanisms responsible for anchoring (see Section III).

### II.3. Anchoring selection

At this point we would like to raise the issue of the selection of anchoring directions which is linked to the occurrence of multistable or degenerate anchorings. Generally speaking, the selection is made by the history of the sample, for instance, by the conditions in which the system is cooled from the isotropic to the nematic phase<sup>23-25</sup> or by the conditions in which the nematic liquid crystal spreads onto the substrate<sup>3,18,26-29</sup>. In the last case, the selected anchoring direction depends on the direction of spreading and, when the anchoring is tilted, on the dynamic contact angle<sup>3,26</sup>. In general, once the selection has been made, it is difficult to change the anchoring direction at a substrate surface. Switching between the two anchoring directions of a bistable anchoring has nevertheless been obtained by applying an electric field<sup>29-31</sup>.

## III. MICROSCOPIC APPROACH - INTERFACE STRUCTURE

### III.1. Interfaces with isotropic and vapour phases

The case of these interfaces is relatively simple in that there is no interaction with a substrate involved. As far as anchoring is concerned, the orientation of the nematic molecules arises mainly from the change in density and order in the interface. The issue is to explain the tilt  $\theta$  of the molecules imposed by these interfaces. Experimentally, it is found that in all the studied compounds the anchoring is tilted ( $0 < \theta < \pi/2$ ) at the nematic-isotropic interface<sup>32-35</sup>. At the free surface there are more differences from one liquid crystal to the other :  $\theta = 0$ <sup>36-38</sup>,  $\theta = \pi/2$ <sup>39,40</sup> or  $\theta$  varying with temperature<sup>10,11</sup>.

Several models have been proposed in order to account for the anchoring at these interfaces, both phenomenological<sup>41-43</sup> and molecular<sup>44-49</sup> ones. Different behaviours are obtained but the problem is to check the validity of all these models. An interesting point is that all the molecular models contain an essential ingredient without which no preferred orientation can be found at nematic-isotropic or nematic-vapour interfaces, namely the coupling between the rotational and translational degrees of freedom of the molecules<sup>50-52</sup>.

The only experimental study of the orientational order at the nematic-vapour interface has shown by means of second-harmonic generation measurements that there is no polar ordering at this interface in 8CB<sup>53</sup>. More work has been dedicated to the positional order at this interface. The presence of the free surface breaks the translational invariance of the nematic phase and



tends to create smectic layers. Such layering has been observed with small angle X-ray reflectivity measurements in several compounds<sup>54-59</sup>. In all cases, the surface structure reflects the local smectic ordering which exists in the bulk nematic phase and becomes long-range when the temperature is lowered to the nematic-smectic phase transition.

### III.2. Interfaces with solid substrates

Only very little is known about the mechanisms producing anchoring on solid substrates. Nevertheless a certain number of experiments give some information about them. On crystalline substrates which are atomically smooth, molecule-substrate interactions must exist which are responsible for the azimuthal orientation of the liquid crystal. Some evidence for these interactions has been given by scanning tunneling microscopy images of monolayers of mesogenic molecules at the surface of cleaved pyrolytic graphite<sup>60-67</sup> and MoS<sub>2</sub> crystals<sup>68,69</sup>. The molecules are physisorbed onto the crystal surface and present a two-dimensional orientational and positional order. The range of molecule-substrate interactions seems to be quite long at least as far as mica is concerned. On mica surfaces coated with Langmuir-Blodgett films of a thickness reaching a few hundred angströms, the anchoring is the same as on non-coated mica surfaces while it changes for greater thicknesses of the films<sup>19</sup>. It has also been shown that the thickness of the mica crystal interacting with the nematic molecules is of the order of 14 Å in muscovite mica<sup>70</sup>.

Molecule-substrate interactions are also responsible for the fact that, on polymer films which have been rubbed by translation on paper or cloth in order to orient the polymer chains<sup>71</sup>, the nematic phase orients parallel to the rubbing direction. Second-harmonic generation measurements have shown that the first monolayer of nematic molecules in contact with such substrates has an anisotropic distribution of the molecules with maxima along the rubbing direction<sup>72,73</sup>. This means that the orientation of the nematic molecules comes from the interaction with the polymer chains which imposes them to be parallel to the chains. Another evidence for the existence of such interaction is that an isotropic polymer film can be made anisotropic by putting onto it a homogeneously aligned nematic liquid crystal<sup>74</sup>.

The different values of tilt of the anchoring direction observed on smooth surfaces are more difficult to explain. On graphite and MoS<sub>2</sub>, the observed planar anchoring directions are obviously due to the fact that the nematic molecules in the first monolayer lay flat onto the substrate<sup>60-69</sup>. But the tilt of

the anchoring directions is not always the one obtained in the first monolayer. Second-harmonic generation measurements have shown that on water and polyimide films, the molecules in the first monolayer make an angle of approximately  $70^\circ$  with the surface normal<sup>72,73,75</sup> while the anchoring is planar on these substrates<sup>76</sup>. The way planar anchoring directions are obtained from the tilted first monolayer is not clear.

When the substrate is covered with a film of surfactant or silane forming a layer of aliphatic chains sticking out of the surface, a possible alignment mechanism is that the nematic molecules penetrate the layer of aliphatic chains. They adopt then the orientation of these chains, which leads to a homeotropic or a conical anchoring depending on the orientation of the chains<sup>12,18,77</sup>. Sum-frequency generation measurements have shown that in this case, the penetrating nematic molecules have an ordering effect on the aliphatic chains<sup>77</sup>. This mechanism can only be valid for non-fully packed layers of aliphatic chains. In the other cases, for instance on OTS<sup>78</sup> layers, the nematic molecules can not penetrate the layer<sup>77</sup>. The homeotropic anchoring observed on OTS-coated glass<sup>76</sup> must thus have a different origin.

Another type of aligning mechanism has to be considered in the case of substrates having a relief as grooved surfaces. Second-harmonic generation measurements have shown that, on rubbed glass and MAP-coated glass<sup>78</sup>, the first monolayer of nematic molecules has an isotropic distribution of azimuthal orientations<sup>72,73</sup>. This means that the molecule-substrate interactions are not responsible for the orientation of nematic liquid crystals parallel to the rubbing direction. On such substrates, the orientation of the nematic phase might come from the fact that this configuration minimizes the elastic distortion of the nematic orientation induced by the presence of grooves created by rubbing. With any other orientations, the molecules have to follow the topography of the grooves which creates a distortion and costs some energy<sup>79</sup>.

Minimization of elastic energy has been proposed as leading to the different anchorings observed on other substrates: inhomogeneous surfaces made of microscopic domains inducing different molecular orientations<sup>80</sup>, SiO films evaporated under oblique incidence<sup>81-84</sup>. In the second case, it has also been shown<sup>21</sup> that order-electricity<sup>42</sup> could play a role.

We have to emphasize that, beside the questions linked to the behaviour of the nematic liquid crystal itself, a major problem arises from the fact that the structure of a lot of substrates obtained by treatment is not well defined and known. In that respect, crystalline surfaces have a great advantage.

#### IV. CONCLUSION

Through all the examples given Section III, one can figure out the diversity of surfaces orienting nematic liquid crystals and the complexity of the phenomena they involve. This is particularly true in the case of interfaces with solid substrates. It appears that in fact, anchoring mechanisms are quite substrate specific. The case of free surfaces and nematic-isotropic interfaces is in principle simpler because the behaviour can depend only on the nematogen. But we have seen that this dependence is quite strong and that anchoring at these surfaces still remains an unsolved problem. Beside the search for the structure of interfaces and the microscopic mechanisms responsible for anchoring, the macroscopic point of view allows to make some predictions about the anchorings induced by a given surface and reveals the existence of anchoring transitions. We have dealt only with the location of the minima of the interfacial energy  $\gamma_s$ . Some studies have also been made about the exact shape of  $\gamma_s$  and the depth of its minima. Unfortunately the interpretation of these measurements remains quite controversial<sup>85-90</sup>.

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