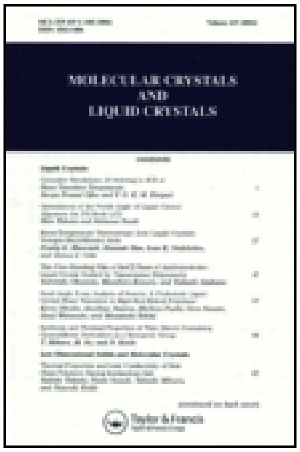

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Anchoring at the Interface Between a Nematic Liquid Crystal and an Isotropic Substrate

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ANCHORING AT THE INTERFACE BETWEEN A NEMATIC LIQUID CRYSTAL AND AN ISOTROPIC SUBSTRATE.

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ABSTRACT: The anchoring properties of the director at the interface between a nematic LC and an isotropic substrate are discussed. More emphasis is devoted to the special cases of the nematic LC free surface and of the nematic-isotropic interface. Some recent theoretical models for these interfaces are briefly discussed and their predictions are compared with the experimental results.

1- Introduction.

Surface interactions establish the orientation of the director **n** at the interface between a nematic LC and an other medium. So far a large effort has been devoted to find physico-chemical treatments of surfaces which induce a well defined and uniform director orientation at the interface. The uniform alignment of the director is , in fact, a fundamental requirement to perform accurate and reproducible measurements on LC. An extended review of surface properties of LC and of Physico-chemical treatments of surfaces has been given in refs.1 and 2. In this paper we briefly review the main orientational properties of the interface between a LC and an isotropic medium. Due to their theoretical relevance , more emphasis is given to the special cases of the nematic free surface and the nematic-isotropic interface.

The director orientation at the interface between a nematic LC (z<0) and an other medium (z>0) is defined by the surface polar angle θ_S and the surface azimuthal angle φ_S as shown in fig.1.

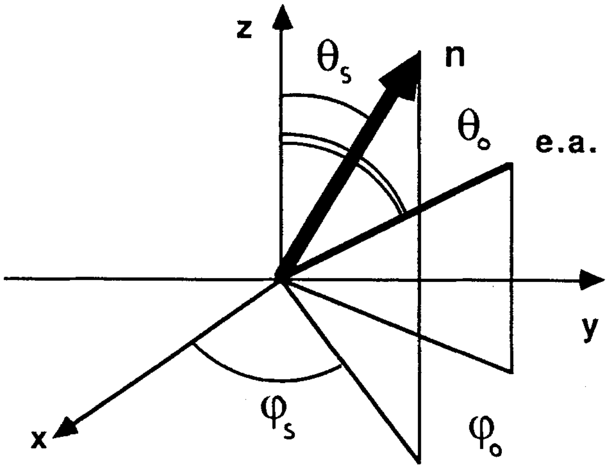

Figure 1: schematic view of the director orientation at the interface . θ_S and φ_S are the polar and azimuthal angles of the director **n**,respectively. θ_O and φ_O are the polar and azimuthal angles of the easy axis (**e.a.**).

The excess of free energy γ per unit surface area depends on the director orientation at the interface and can be written as

$$\gamma = \gamma(\theta_O,\varphi_O) + W(\theta_S-\theta_O,\varphi_S-\varphi_O) \qquad (1)$$

where θ_O and φ_O correspond to the values of the polar and azimuthal angles which minimize the γ-function (easy axis), whilst W is a positive function termed "anchoring energy function". At the equilibrium and in the absence of external torques, $\theta_S= \theta_O$ and $\varphi_S=\varphi_O$. The anchoring energy function represents the work which must be spent to rotate the director from the easy axis direction to the actual one. The azimuthal and polar anchoring torques per unit surface area are, respectively : $\tau_a=- \partial\gamma/\partial\varphi_S$ and $\tau_p=-\partial\gamma/\partial\theta$. Near the equilibrium position these torques are approximatively given by $\tau_a=- 2\, W_a(\varphi_S-\varphi_O)$ and $\tau_p=-2\, W_p(\theta_S-\theta_O)$, where:

$$W_a = \frac{1}{2}\frac{\partial^2\gamma}{\partial\varphi_S^2}\bigg|_{\varphi_{o,}\theta_o} \qquad (2)$$

and

$$W_p = \frac{1}{2}\frac{\partial^2\gamma}{\partial\theta_S^2}\bigg|_{\varphi_{o,}\theta_o} \qquad (3)$$

are the polar and azimuthal "anchoring energy coefficients", respectively. Typical experimental values of W_a and W_p lye in the range[1] 10^{-4} erg/cm^2- 10^{-1} erg/cm^2.

2- Interface between a nematic LC and an isotropic medium .

In this paper we concentrate our attention on isotropic substrates. In this case the surface free energy γ does not depend on the director azimuthal angle (W_a=0). Due to the symmetry of the interface , the function γ can only depend on the scalar product **n.k** = $\cos(\theta_S)$ between the director **n** and the normal **k** to the interface. Therefore γ can be expressed as a Taylor power expansion in terms of $\cos(\theta_S)$:

$$\gamma(\theta_S) = \gamma'_0 + \gamma'_1\cos\theta_S + \gamma'_2\cos^2\theta_S + \ldots\ldots + \gamma'_n\cos^n\theta_S + \ldots \quad (4)$$

Barbero et al.[3] showed that eq. (8) is not useful from the practical point of view since the expansion terms are not orthogonal functions. This means that the coefficients obtained from the experiments by truncating the expansion to a given order depend on the truncation order. Therefore they propose alternative power expansions in terms of orthogonal functions. The most simple one is the Fourier expansion:

$$\gamma(\theta_S) = \gamma_0 + \gamma_1\cos\theta_S + \gamma_2\cos 2\theta_S + \ldots\ldots + \gamma_n\cos n\theta_S + \ldots \quad (5)$$

Note that the odd coefficients (γ_{2n+1}) in eqs.(4) and (5) must vanish for non ferroelectric systems. Nematic LC are well known to be non ferroelectric systems for what concerns bulk properties. However near the surface the translational symmetry of the system is broken and a surface ferroelectricity may occur[4] . Surface polar effects have been introduced by Mayer et al.[5] to explain spontaneous splay distortions observed in freely suspended smectic films. More recently P.Guyot-Sionnest et al.[7] used a very sensitive optical method (second harmonic generation) to probe the surface electric polarization at the interface. Direct evidence for a surface polarization was found in the case of a 8CB monolayer on water and on a DMOAP-coated glass substrate, whilst no polarization was found for the free surface of 8CB. So far the effective relevance of surface polarity on the orientational properties of the interface has not been investigated and usually a non polar behaviour of the surface ($\gamma_{2n+1}=0$) is assumed. Furthermore many authors use for the surface free energy the Rapini-Popoular expression:

$$\gamma(\theta_s) = \gamma'_o + W_p \cos^2 \theta_s \qquad (6)$$

which corresponds to stopping eq.(4) to the first two non-vanishing terms. In this simplified case the polar anchoring coefficient given by eq.(3) coincides with the "anchoring energy" defined as the work which needs to rotate the director from the stable equilibrium position to the unstable one . Notice, however, that , in the general case, these two parameters do not coincide although in the literature the same confusing term of "anchoring energy" is often used to indicate both them.

3- Experimental measurements of the anchoring energy function .

The measurements of anchoring energy have been often performed by measuring the threshold field H_c' for the Freederickz transition[7] in a thin nematic layer of thickness d. Due to the finite value of the anchoring energy, the threshold field is lower than the value H_c predicted for strong anchoring. The relative difference $\delta=(H_c-H_c')/H_c$ gives a direct measure of the anchoring energy coefficient. However, in the case of strong anchoring, H_c and H_c' slightly differ the one from the other and thus, small experimental uncertainties on their values can produce large errors on δ and W_p[2,7]. Furthermore measurements of the threshold field only furnish the anchoring energy coefficient W_p. Therefore this kind of measurements do not give any information about the effective angular dependence of γ. Other experimental methods to measure the anchoring energy are discussed in refs.1 and 2.

In recent years some authors attempted to detect experimentally the correction terms to eq.(6) by using different experimental methods. The methods to measure the anchoring energy function consist on exerting a known torque per unit surface area τ_e on the director and on measuring the corresponding rotation of the director at the interface. Due to the external torque the director rotates until a new equilibrium angle $\theta_s=\theta_o$ is reached where the restoring anchoring torque τ_p balance the external one. Therefore the function $\gamma(\theta_s)$ can be obtained by measuring the surface director angle θ_s versus the external surface torque $\tau_e = -\tau_p = \partial\gamma/\partial\theta_s$. The surface polar torque is usually generated either by applying an external magnetic[8](or electric[9]) field or by sandwiching the nematic LC between two solid plates giving different director orientations[10] (hybrid aligned cell (HAN)). In all these cases the director-field near the interface exhibits a distortion which produces a surface elastic torque on the director given by:

$$\tau_e = K(\theta_s) \left.\frac{\partial\theta}{\partial z}\right|_{z=0} \qquad (7)$$

where $K(\theta_s) = K_{11}\sin^2\theta_s + K_{33}\cos^2\theta_s$ and K_{11} and K_{33} are the splay and bend elastic constants[11], respectively. The value of $\partial\theta/\partial z$ and the corresponding surface elastic torque for a given experimental geometry can be calculated by using the Leslie-Enricksen[11] elastic equations for the director. The surface polar angle θ_s can be obtained by using transmitted light methods, reflected light methods or capacitive methods[1,2]. We point out that a special caution must be devoted to measure the anchoring energy by using electric fields since , in this case, many effects as , for instance, space charges, electrohydrodynamic motions , flexoelectricity and surface polarization may affect the experimental results.

In order to estimate the strength of the anchoring torque it is convenient to introduce the polar "extrapolation length" $b=K/2W_p$, where K is an average elastic constant of the nematic LC . This length has to be compared with the characteristic length ξ of the director distortion in the bulk. If $b \ll \xi$ the external torque is not able to modify appreciably the surface director angle (strong anchoring) which then explores the region near the bottom of the surface free energy well. In this case the anchoring energy coefficient only can be obtained from the measurements and it is not possible to detect any difference between the simple Rapini-Popoular expression of eq.(6) and the more general one of eq.(5). In order to make the experimental comparison between different expressions of the surface free energy the condition $b > \xi$ has to be satisfied either by using weak anchoring plates(large b-values) or by applying very strong external torques(large ξ- values). Up to a few years ago the experimental measurements of anchoring energies only concerned the anchoring energy coefficient . More recently measurements of the θ-dependence of the surface free energy have been performed in weakly anchored cells by using high intensity magnetic fields[8] (H>30 KG), electric fields with nematic LC having high dielectric anisotropy[9] and low thickness hybrid aligned nematic cells[10]. In all these experiments departures from the simple Rapini-Popoular expression were found. However Barbero et al.[12] analyzed these experimental results and showed that flexoelectricity and ordoelectricity may produce apparent departures from the Rapini-Popoular expression of the same kind of the measured ones. Therefore at the present time no unambiguous measurement of the higher order terms in eq.(4) and in eq.(5) has been yet reported. In particular more detailed experimental investigations need in order to clarify the effective role played from flexoelectricity and ordoelectricity. At this regard it should be interesting to investigate the case of the azimuthal anchoring for which ordoelectricity and flexoelectricity do not play any role.

4- The free surface of nematic LCs: Experimental results.

Molecular theories of the interfacial anchoring are very complex and so far more attention has been devoted to study the simplest cases of the nematic LC-vapour interface (free surface) and of the interface between anisotropic and isotropic phase of the nematic LC (nematic-isotropic interface). Therefore experiments on these interfaces represents an important test for molecular theories of the anchoring. Unfortunately the experimental measurements in this field are very few and often concern the nematic-air interface where surface contaminants ,as water vapour, can affect the surface anchoring (see, for instance, J. Prost[13]). Let's now summarize briefly the main experimental results on free surfaces of LC.

A planar alignment of the director (θ_s=90^o) has been observed both at the free surface[14] and at the nematic-air interface[15,16] of the nematic LC

PAA, whilst a homeotropic orientation (θ_s=0) has been observed at the free surface[17] and at the nematic-air interface[18-20] of some cyanobiphenils (nCB; n=5-8). A more interesting behaviour has been found for the nematic-air interface[16] and the free surface[21,22] of the nematic LC's MBBA and EBBA. In both these cases the director orientation is tilted ($\theta_s \sim 25^o$) and greatly depends on the temperature T. Very thick samples of MBBA and EBBA exhibit a second order orientational transition at the free surface when the temperature reaches a critical value T* slightly below the clearing value T_{ni} (T_{ni}-T*= 0.6^o C). In the corrispondence of the critical temperature, the director polar angle and the anchoring energy go to zero according to the critical behaviours: $\theta_s \propto (T^*-T)^{1/2}$ and $W_p \propto (T^*-T)$. A similar behaviour has been observed for the temperature dependence of the director polar angle at the free surface of the nematic LC EBBA[21]. The anchoring energy coefficient has been also measured many years ago by Perez et al.[18-19] in the case of a thin layer of 5CB floating on water. The easy orientation at the water-nematic interface was found to be planar and a transition to a uniform planar alignment on the whole layer was observed when the thickness became lower than a critical value $d_c \sim 2$ μm. From the experimental results the authors estimated the anchoring energy coefficient $Wp \sim 4.5 \times 10^{-3}$ erg/cm^2. More recently Palleschi[17] attempted to measure the anchoring energy coefficient at the nematic-vapour interface of some cyanobiphenils(nCB, n=5-8) by measuring the variation of the surface director angle produced by a 8 KG horizontal magnetic field. No variation was observed within the experimental noise and thus a lower limit $W_p = 6 \times 10^{-2}$ erg/cm^2 was estimated for the anchoring energy coefficient . The large discrepancy between these two values of the anchoring energy coefficient is probably due to the different nature of the two interfaces (nematic-air, nematic-vapour). Measurements concerning the anchoring energy at the nematic-air interface of 5CB have been also performed by Warenghem[20] on nematic layers floating on liquid gallium or on a glass plate. These latter experiments clearly show that the anchoring energy can greatly change from point to point on the nematic-air interface due to surface contamination.

A more complex behaviour has been observed in freely suspended layers of MBBA[23,24] and EBBA[24] in the presence of air atmosphere. Three different director arrangements have been observed depending on the film thickness. The low thickness structure (LTS , $d < 10\ \mu m$) is characterized by an uniform tilt of the director everywhere in the film; the intermediate thickness structure (ITS , $d \sim 15\text{-}50\ \mu m$) is characterized by an uniform homeotropic alignment, whilst the high thickness structure (HTS , $d > 60\ \mu m$) exhibits a spontaneous splay of the director across the film layer. In this latter case the director orientation changes gradually from the almost homeotropic surface orientation to an almost planar alignement in the bulk[23] whithin a thickness of the order of 50 μm. A second order transition from the LTS to the ITS occurs at a given critical thickness d_c , whilst the transition from ITS and HTS is continuous and no threshold thickness is observed. The transition between LTS and ITS is observed also if the thickness of the layer is fixed and the temperature is changed. If one starts from the LTS , the polar angle θ_s decreases by increasing the temperature and vanishes as the temperature exceeds a critical value T'. This latter critical temperature is a decreasing function of the film thickness. The critical thickness and the critical temperature depend perhaps on the curvature of surfaces and also on the water vapour content of air. For this reason measurements on freely suspended films in equilibrium with their vapour should be desirable. Fig. 2a shows the temperature dependence of θ_s^2 for a fixed thickness value, fig.2b shows the thickness dependence of θ_s^2 for a fixed temperature and fig.2c shows the dependence of the critical thickness d_c on temperature. It is important to remark that, due to surface contaminants, the absolute values of the critical thickness $d_c(T)$ can largely change from experiment to experiment but the qualitative dependences of figs. 2 are always observed.

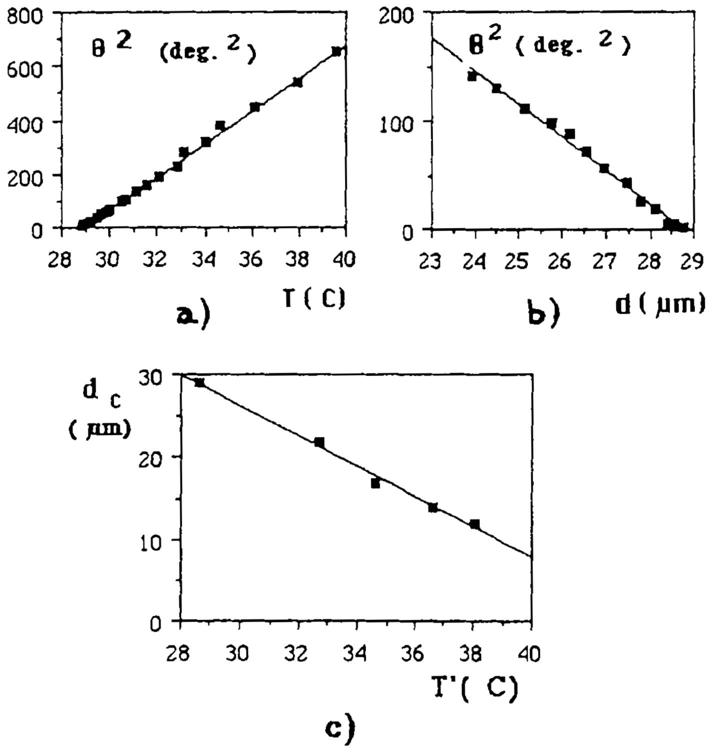

Figure 2: 2a) Temperature dependence of θ_s^2 for a freely suspended nematic layer of thickness d=29 μm ; 2b) Thickness dependence of θ_s^2 for T= 28.6 °C; 2c) critical thickness d_c versus the critical temperature T'. Full lines correspond to the best linear fits.

For what concerns the nematic-isotropic interface, two different experimental methods have been used to obtain stable nematic-isotropic interfaces. In the first one[25-27] a thick nematic sample (d=2-4 cm) is enclosed between two parallel plates maintained at two different temperatures T_1 and T_2 ($T_1<T_{ni}<T_2$). Then a plane and stable nematic-isotropic interface develops in that region of the sample where $T=T_{ni}$. In the second case[28-29], a thin doped nematic layer is sandwiched between two parallel plates treated in such a way that wetting from the anisotropic

phase occurs on the lower plate(PVA-coated plate) and wetting from the isotropic phase occurs on the upper plate(SiO_2-coated plate). At the clearing temperature a planar nematic-isotropic interface appears. Table I summarizes the experimental results for the nematic isotropic interfaces of MBBA and some cyanobiphenils.

	θ_0 (deg.)	W_p (10^{-4} erg/cm^2)	γ_{eq} (10^{-2} erg/cm^2)
MBBA	14 + 3 (25,26) 25 + 3 (25,26)		2.2 + .4 (25) 2 + .7 (47) 1.6 + .7 (48)
5CB	63.5 +6 (27) 61.9 + 6 (28)	4.8 + 1.2 (27) 5 (28)	1.5 + .4 (47) 2.1 (29)
6CB	64.5 + 6 (27)	.84 + .2 (27)	71 +.4 (47)
7CB	52.6 + 6 (27)	8.3 + 2.2 (27)	1.82 +.7 (47) 2.8 + 1.2 (49)
8CB	48.5 + 6 (27)	8.5 + 2.1 (27)	.95 + .4 (47)

Table I : Experimental results for the easy tilt angle θ_0, the anchoring energy coefficient W_p and the interfacial surface tension γ_{eq} of the nematic-isotropic interfaces of MBBA and n-CB(n=5-8). The two reported values for MBBA correspond to measurements on two different specimens. The anchoring energy coefficient for 5CB given in ref.28 corresponds to a definition of the anchoring energy which differs by a factor 2 with that of eq.(3). Therefore the value reported in table I has been rescaled according to the definition of eq.(3).

5- Theoretical models of the interfacial anchoring.

In the last years many phenomenological[30-36] or molecular theories[38-43] of the interfacial anchoring have been proposed. All models predict the planar easy alignment, whilst few of them are able to explain the homeotropic and the tilted alignments. Mada and Kobayashi[31] explained the tilted alignment by introducing terms dependent on the surface derivatives of the director in the phenomenological expression of the surface free energy . However, as Barbero et al.[33,45] showed, surface derivative terms make unsolvable the corresponding variational problem. Parsons[4] explained the tilted alignment as due to the competition of polar and non-polar interactions by proposing the phenomenological expression:

$$\gamma = \gamma'_0 + \gamma'_1 \cos \theta_s + \gamma'_2 \cos^2\theta_s \qquad (8)$$

Depending on the values of the phenomenological coefficients γ_1 and γ_2 , homeotropic, planar and tilted easy alignments can occur and a second order phase transition from tilted to homeotropic alignment is predicted when γ_1=-2γ_2. More recently Sluckin and Poniewierki[36] showed that the assumption of polar interactions is not necessary to predict the director tilt and proposed a power expansion of the surface free energy in terms of the surface order parameter Q_{ij} in analogy with the Landau-De Gennes model . By assuming no polarity at the interface and by truncating the expansion to the quadratic contributions they obtained :

$$\gamma = \gamma_0(Q) + \gamma'_2(Q) \cos^2 \theta_s + \gamma'_4(Q) \cos^4\theta_s \qquad (9)$$

where Q is the surface scalar parameter[11]. The most appealing aspects of this theory are its capability of describing both the orientational properties of the interface and the surface order phenomena[28,29] (wetting transitions) and its strict relation with the Landau-De Gennes theory of the bulk free energy. Furthermore this theory holds for every kind of interface between a nematic LC and an isotropic medium. This theory ,too, predict homeotropic,planar and tilted easy alignments and surface orientational first and second order transitions depending on the values of the coefficients γ_2(Q) and γ_4(Q).

Phenomenological models do not allow to obtain quantitative predictions and do not indicate what are the physical mechanisms responsible for a given director orientation. A different approach consists on calculating the surface free energy starting from the microscopic interactions between molecules. These calculations are very complex and thus, so far only simple interfaces as the free surface and the nematic-isotropic interface have been investigated. Furthermore drastic simplifications are made in order to obtain analytical expressions (step change in density and order parameter near the interface and decoupling between translational and rotational order (mean field approximation)). Van der Waals interactions have been found[38-40] to favour a planar orientation of the director at the free surface as observed for PAA and thus, they cannot explain the experimental results for MBBA, EBBA and cyanobiphenils. In a recent paper[41] Sullivan calculated the mean field surface free energy by expressing the generic interaction between axially-symmetric molecules as a power expansion in spherical harmonics. He showed that Van der Waals forces cannot explain the tilted alignment, whilst quadrupole-quadrupole interactions and short range interactions produce a surface free energy of the same kind of eq.(9). Therefore short range interactions and quadrupolar ones can explain all the experimental results. Kimura et al.[42] and Holyst et al.[43] investigated directly the role of short range hard rod interactions by extending the Onsager approach to the case of the interface. Both them found that short range interactions favour the homeotropic alignment at the free surface, whilst for what concerns the nematic-isotropic interface, a easy planar alignment is predicted by Kimura and a tilted alignment at the angle $\theta_s=60^o$ is found by Holyst. In this latter case the director angle is found to be independent on the length to width ratio of the spherocilinders , whilst the anchoring energy coefficient greatly reduces as this ratio tends to zero.

A different approach has been recently proposed by Barbero et al.[37] which showed that an electric polarization of the medium occurs if space variations of both the director-field (ferroelectricity) and the scalar order parameter(ordoelectricity) are present. This polarization is strictly related to the presence of a nonvanishing average electric quadrupole proportional to the order parameter tensor[37,44]. Near the interface the order parameter exhibits a strong variation and thus, a surface polarization occurs. The free energy is minimized when the director angle θ_S is equal to the magic angle $\theta_S=54.7^o$ which agrees very well with the experimental results for the nematic-isotropic interface of 7CB. By making the resonable assumption that ordoelectric coefficients are of the same order of magnitude of flexoelectric ones, they also obtained a satisfactory quantitative agreement with experimental measurements of the anchoring energy coefficient at the nematic-isotropic interface of 7CB.

6 - Conclusions.

In these latter years the understanding of surface polar anchoring at the interface between a nematic liquid crystals and an isotropic medium has greatly progressed. In particular it is now well established that the tilted easy orientation can be explained by short range interactions(quadrupolar and hard rod). Furthermore new accurate experimental methods to measure the entire angular dependence of the surface free energy have been developed. However more experimental results on a more extended class of nematic LC's need in order to make a complete comparison between the different theoretical models. In particular many questions need a further clarification and between them: a) what is the relative importance of quadrupolar and hard rod interactions? b) do polar contributions , as those introduced by Parsons, play some role on surface properties? ; c) What is the influence of surface elastic constants on the anchoring energy[45]?; d) What is the influence of wetting phenomena on the surface anchoring[46]? e) how the orientational regimes of freely suspended layers of MBBA and EBBA can be explained? Are these regimes related to a competition between long range and short range interactions as discussed in some theoretical papers by E.Dubois-Violette and P.G.De Gennes[34]?

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