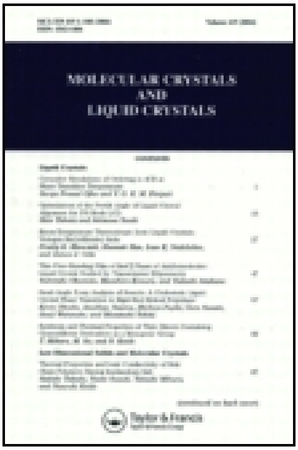

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THE INTERFACIAL LAYER OF INORGANIC SOLID SURFACES AND LIQUID CRYSTALS-IMPLICATION ON THE ANCHORING ENERGY

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Presented at the 10th Freiburger Arbeitstagung Flüssigkristalle, 26.3.1980

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Abstract: Liquid crystal anchoring energy varies with the distance to the solid substrate in the interfacial layer. Experimental values correspond to a low anchorage as the liquid crystal slides on its interfacial layer. The question of whether it will be possible to observe low anchorage in a parallel alignment is raised.

From theoretical computation it has been suggested that low anchoring energy of nematic liquid crystals (L.C.) on solid substrates would allow an increase in the multiplexing capability of Twisted Nematics displays by a factor of four (1).

Following Kleman (2) the anchoring energy W_1 is phenomenologically expressed as the sum of an isotropic energy term W_o, an in plane (torsion) anchorage W_ϕ and an out of plane (azimuthal) anchorage W_θ.

$$W_1 = W_o + W_\phi + W_\theta \quad (I)$$

where the angular definition is indicated on fig. 1. The angular dependence of W_1 is mathematically written:

$$W_\phi = B_\phi \sin^2\phi \quad (II)$$

$$W_\theta = W_o + B_\theta \sin^2\theta \quad (III)$$

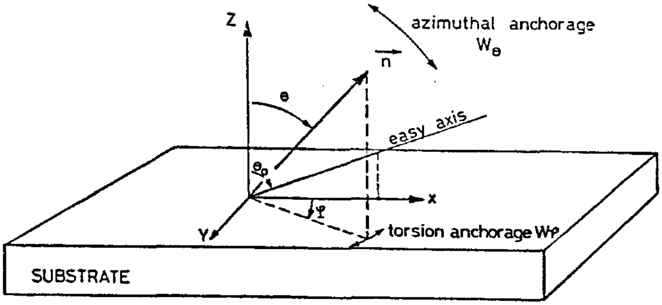


Fig. 1 Coordinate geometry - Definition of the torsion and azimuthal anchorage

The L.C. anchorage on a solid substrate results from physico-chemical interactions whose energy may be theoretically obtained from the two phases' surface tension.

When a liquid of surface tension γ_{LV} comes into contact with a solid of surface tension γ_{SVo} an interfacial layer builds up whose energy γ_{SL} (identical to W_1) is

$$\gamma_{SL} = \gamma_{SVo} + \gamma_{LV} - W_a \quad \text{(IV)}$$

where γ_{SVo} is the solid surface tension at equilibrium with the liquid saturated vapour [which is related to the solid-vacuum interface free energy γ_S and the adsorbed liquid layer surface pressure π_o by $\gamma_{SVo} = \gamma_S - \pi_o$ (V)]
and W_a is the adhesion energy which may be approximated (3) by

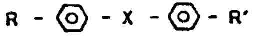
$$W_a = 2\sqrt{\gamma_{SVo}\,\gamma_{LV}} \quad \text{(VI)}$$

Solid surface energy γ_S is not directly measurable and depends on the surface preparation and history, but for inorganic substrates is calculated to be over 0.2 JM^{-2} in agreement with values obtained from heat of immersion measurements (3). For polar liquids, surface pressure π_o exceeds 0.1 JM^{-2}; the resulting γ_{SVo} value is in any case over 710^{-2} JM^{-2} (4) which corresponds to the surface tension of an inorganic substrate covered with water layers. Some authors consider that the first molecular layer in contact with inorganic substrates is a water layer which is not displaced by the L.C. molecules (4).

In the case of a liquid of $\gamma_{LV} = 310^{-2}$ JM^{-2} which is typical for L.Cs (table 1) the interfacial layer energy γ_{SL} is obtained from (IV - VI): $\gamma_{SL} = 810^{-3}$ JM^{-2}.

TABLE 1

Surface Tension of Nematic Liquid Crystals



X	L.C.	γ_L	Ref.	Method	Remarks
					γ_L of MBBA impossible to measure accurately (17)
SCHIFFBASE	MBBA	38 (23°C)	5,6	?	$\gamma_d = 29$ $\gamma_p = 9$ (5)
		35.8	7	III	$\gamma_{/\!/} = 34$ $\gamma_\perp = 26$ (7)
		35.3	8		
		34	9,10	I, II	$\gamma_d = 33$ $\gamma_p = 1$ (10)
		32 - 34	11	II	corr. uncorrected
		32.6*	12	II	$*\gamma_L = 28.8$ corr. Harkins and Jordan (12)
		30	13	I	
	80 MBBA/ 20 BBCA	35.5	10	II	$\gamma_d = 34$ $\gamma_p = 1.5$
STILBENE	BECS	35.7	7	III	
ESTER $\Delta\epsilon < 0$	MPPB	24.5	9	I	
	EN 18	27.5±0.5	14	III	
$\Delta\epsilon > 0$	HCPB	27	9	I	
	ROTN 103	27.5±0.3 (22°C)	14	III	
AZOXY	PAA	38 (125°C)	15	V	$\gamma^d_{/\!/}$(calc) = 37.8 $\gamma^d_\perp$(calc) = 44.6 (16)
		37 (120°C)	8		
	PAP	31.2 (145°C)	15	V	
	ZLI IV	37.3	7	III	
TOLANES	MPT + PHT	25	9	I	not aligned on plasma PTFE ! (9)

TABLE 1 (continued)

X	L.C.	γL	Ref.	Method	Remarks
BIPHENYLES	5 CB	30	9	I	
		28.1 (31.5°C)	17	I	
		27.9 (20°C)	17	I	
	8 CB	26.2 (41°C)	17	I	
	E 7	29.3 (22°C)	14	III	
	E 8	30.6±0.2 (22°C)	14	III	
PHENYLCYCLOHEXANE	ZLI 1132	31±0.5 (22°C)	14	III	difficult to align homeotropically (14)

L. C. Code		
MBBA	4 Methoxybenzylidène-4'-n-butylaniline	
BBCA	4 Butoxy-benzylidène-4'-cyano aniline	
PAP	para azoxy-phenetole	
BECS	4 n-butyl-4'-ethoxy α chlorostilbène	
ZLI IV	4 Methoxy-4'-butylaxozybenzène isomers mixtures (Merck)	
ROTN 103	Roche Ester mixture	
MPPB	4 Methoxy-4'-Pentyl Phenyl Benzoate	
EN 13	Chisso mixture (high negative dielectric anisotropy)	
HCPB	4 Heptyl-cyano-biphenyl	
MPT	4 Methoxy-4'-Pentyl tolane	eutectic
PHT	4 Propyloxy-4'-Heptyl tolane	
PAA	para-azoxy-anisole	
5CB	4 pentyl-4'-cyanobiphenyl	
8CB	4 octyl-4'-cyanobiphenyl	
E7, E8	BDH eut. mixture	
ZLI 1132	Merck eut. mixture	

Methods	
I	Wilhemy plate
II	de Nouy ring
III	Hanging drop
IV	Contact angle
V	Capillary

The dimension of the interfacial layer is not precisely known, but from double layer theory it extends at least over 100 A° in a resistive liquid.*

From the interfacial energy profile as sketched in fig. 2, one sees that the interfacial or anchoring energy varies with the distance from the surface.

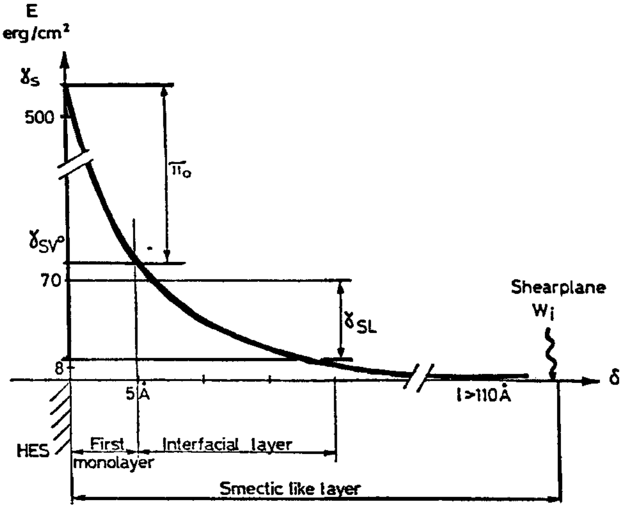


Fig. 2 The solid - L.C. interfacial layer. Interfacial interactions form a smectic-like layer. The L.C. slides on its interfacial layer under constraint at a shear plane.

In nematic liquid crystals, the excess energy of the interfacial layer produces a higher ordering of the L.C. which is observed in an L.C. layer enclosed between two glass covers as an adherent film which moves with the glass plates when they are translated (18).

This adherent superficial film of L.C. is often described as a smectic-like layer (17). The order parameter is estimated to exceed its bulk value over 1 μ at the air L.C. interface and 100 A° at the solid/L.C. interface (19). The nematic orientation leads to an aniso-

* After completion of this paper, contributions presented at the Kyoto International conference by G.I. Sprokel on the one hand and J.N. Israelachvili et al, on the other hand show that the interfacial layer thickness is below 1000 A° and above 200 A° for biphenyl L.C.'s.

tropic interfacial energy which determines the L.C. anchoring.

As surface tension acts as a force normal to the substrate, there is no dependence of the interfacial energy on the in-plane orientation of the molecules.

The torsion anchorage W_ϕ results from substrate non uniformity which may be controlled, for instance, by uniform grooving of the surface (fig. 3) in which case W_ϕ may be calculated (20):

$$W_\phi = \frac{K}{4} A^2 q^3$$

where K is the L.C. elastic constant and other symbols are defined on fig. 3.

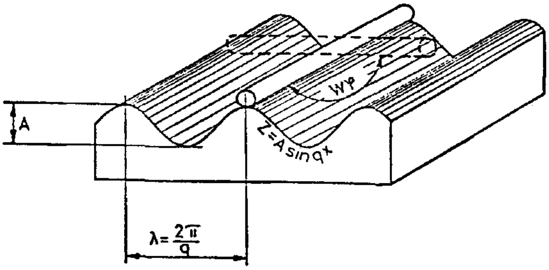


Fig. 3 Torsion anchorage on a grooved surface

W_ϕ may also be roughly estimated from the width δ of surface disclination lines (21)

$$W_\phi = \frac{\pi^2}{2}\frac{K\delta}{d^2}$$

(where d is the L.C. layer thickness), or measured from twist angle variation in a twisted layer submitted to a magnetic field (22).

Calculated and experimental values are compared in table 2.

Table 2 Calculated and experimental values of W_ϕ (1 erg/cm^2 = 10^{-3} JM^{-2})

Substrate	W_ϕ calc (JM^{-2})*	W_ϕ exp (JM^{-2})
Glass	-	5.10^{-6} (21)
Rubbed Glass	8.10^{-5}	$\left\{\begin{matrix} 7.10^{-6} \\ 10^{-4}\end{matrix}\right.$ (22)
SiO$_x$ evap 30°	5.10^{-4}	10^{-3} (2)
Heptylamine on Glass	-	$\sim 5.10^{-5}$ (13)
Trimethyl chlor. silane on Glass	-	$\lesssim 5.10^{-6}$ (13)

* $W_\phi = \frac{1}{4} K A^2 \phi^3$ (1)

Weak anchorage $\sim$ NkT = 210^{-7} JM^{-2}

(N molecular surface density)

The orders of magnitude seem to be in agreement, and in any case the torsion anchoring energy is higher than the bulk twist energy $W_{twist} = \frac{K\phi_T^2}{2d} \sim 10^{-6}$ JM^{-2} (ϕ_T twist angle). Thus in equation (I) the only term related to the anisotropy of the L.C.'s surface tension is the azimuthal anchorage W_θ which is equal to the difference in interfacial energy between the L.C. parallel and perpendicular oriented layers.

Let ξ (0) and ξ $(\frac{\pi}{2})$ be the values of the physical property ξ in both orientations

$$W_\theta = w_o + B_\theta \sin^2\theta = \gamma_{SL}(0) + |(\gamma_{SV}(\tfrac{\pi}{2}) - \gamma_{SL}(0)| \sin^2\theta$$

in equation IV-VI, πo, γ_{SL} and W_a are θ dependent

$$B_\theta = \gamma_{SL}(\tfrac{\pi}{2}) - \gamma_{SL}(0) = [\pi_o(0) - \pi_o(\tfrac{\pi}{2})] + [\gamma_{SV}(\tfrac{\pi}{2}) - \gamma_{SL}(0) + (W_a(0) - W_a(\tfrac{\pi}{2})] \quad \text{(VIII)}$$

Although there are no reliable data on these values for L.C.'s, we will try to get an order of magnitude :

No account has been taken of the surface pressure in the literature. As on inorganic substrates, L.C. prefer to be parallel to the substrate, $\pi_o(0) > \pi_o(\frac{\pi}{2})$ but the anisotropy is not expected to be large.

L.C. surface tension anisotropy $\gamma = \gamma_{SL}(0) - \gamma_{SL}(\frac{\pi}{2})$ is estimated to be + 4.5 10^{-5} JM^{-2} for MBBA (23) and 5 10^{-6} JM^{-2} for 5CB (24), although calculated values give higher values of opposite sign (16) (25).

The difference in adhesion energy W_a between the parallel and perpendicular orientation has been deduced from experimental data at the glass/MBBA interface to be 6.2 10^{-3} JM^{-2} (24) and is calculated to be 7.16 10^{-3} JM^{-2} for PAA on glass (16).

Thus the energy in the interfacial layer is mainly determined by the adhesion energy, and from VIII one gets for the azimuthal anchorage

$$B_\theta = \gamma_{SL}(0) - \gamma_{SL}(\frac{\pi}{2}) \sim W_a(o) - W_a(\frac{\pi}{2}) = 6 10^{-3}\ JM^{-2}$$

This large difference of surface energy means that the orientation of the interfacial layer cannot be modified by elastic deformation of the L.C. where the energy is at most 10^{-5} JM^{-2}.

In that case, as suggested by Parsons (25) one should not, in calculations, minimize the bulk plus surface energy, but minimize the bulk energy and require the boundaries conditions to be satisfied at the surface. A L.C. layer of thickness d, homeotropically oriented and submitted to a magnetic field directed parallel to the substrate will change its orientation beyond a distance d_c:

$$d_c = \frac{3K}{2\ (\gamma(\frac{\pi}{2}) - \gamma(0))} \qquad \text{(IX)}$$

as observed by Naggiar (26) on a homogeneously aligned drop of PAA deposited on a hole drilled in a crystal sheet, submitted to a magnetic field perpendicular to the substrate. Experimentally azimuthal anchorage energies are either estimated from surface disclination lines (2) (13) or measured by magnetic deformation of homeotropically oriented layers where IX should apply. The experimental B_θ values obtained are weak and comparable to the L.C. surface tension anisotropy (table 3). This difference between the estimated and experimental values would correspond to the deformation of the L.C. layer at a distance from the surface at which the L.C. is not affected by the surface potential. At this shear plane the energy of the immobilised layer is W_i and $B_\theta \sim \gamma(0) - \gamma(\frac{\pi}{2})$.

TABLE 3

Experimental Values of B_θ

$$W_\theta = W_o + B_\theta \sin^2\theta$$

Substrate	C. L.	B_θ ($10^{-6}JM^{-2}$)	Method	Ref.
Air	5 CB	4	D.A	24
Si Ox (30° + 5°)	6 CB	2.1	Δ n	27
Glass + $R_nN\ {}^+Me_3\ X^-$	MBBA	3	M.D	23
Glass + $NH_2C_nH_{2n+1}$	MBBA	2	M.D	22
Glass + $NH_2 - C_7\ H\ 15$	MBBA	2.6	S.D	13
Glass + Lecithin	MBBA	3	M.D	23
Glass + DMOAP	MBBA	6	M.D	23
In_2O_3 + DMOAP	MBBA	10	M.D	23
In_2O_3 + Lecithin	MBBA	6	M.D	23
$In_2O_3 + NH_2\ C_{16}\ H_{33}$	MBBA	3.5	M.D	23

MBBA $\gamma_{/\!/} - \gamma_\perp \sim 4.5\ 10^{-5}$ (22)

5 CB $\gamma_{/\!/} - \gamma_\perp \sim 5\ 10^{-6}$ (23)

D.A	differential alignment
Δ n	birefringence of the superficial layer
M.D	magnetic deformation
S.D	surface disclination

On inorganic layers where L.C. align generally parallel to the substrate, although the anchorage is strong ($B_\theta \sim 610^{-3}$ JM^{-2}), weak interactions are measured as the perturbed part of the nematic layer interacts with its smectic-like interfacial layers. The same situation is probably observed on most surfactant adsorbed layers. Even with $B_\theta \sim 510^{-6}$ JM^{-2} the anchorage parameter $\lambda = \frac{\pi K}{B_\theta d}$ of ref. 1 is about 1 for a L.C. of $K \sim 10^{-11}$ N and cell thickness d = 10 μ.

The value of γ_s^o at the solid surface as shown in fig. 2 for x = 0 does not influence the value of the energy W_i at the shear plane as long as $\gamma_s^o > W_i$. Thus the effective anchoring energies measured on polymeric or inorganic surfaces are comparable. On fig. 4 are reported voltage-capacitance curves for 10 μ L.C. layers enclosed between two conductive glasses whose surface has been treated in order to have different anchoring energy from literature data. One sees that the theoretically expected (1) variations of threshold voltage or slope are not observed.

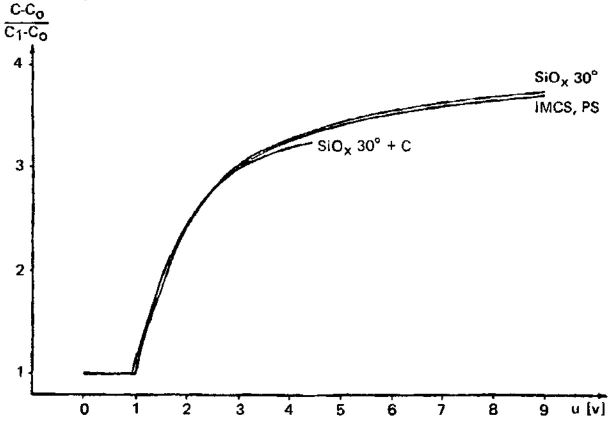


Fig. 4 Reduced capacitance vs. voltage of a 10 μ cell whose inner walls are coated with different aligning layers. L.C.: E7 - homogeneous state.
C_o capacity of empty cell
C capacity at 0 Volt

SiO_x30^o : obliquely evaporated SiO_x layer (strong anchorage)
SiO_x30^o+C : above layer exposed in a flame of acetylene ($B_\theta = 0.1\ 10^{-7}$ JM^{-2}, ref. 2)
TMCS trimethylchlorosilane ($B_\theta = 1.5\ 10^{-6}$ JM^{-2}, ref. 13)
PS rubbed 1000 A° polysulfone layer

Weak anchoring would suppose $\gamma_S \lesssim W_i$, that is, similar energy of the solid - L.C. and L.C. - L.C. interactions as already noted by de Gennes (28). But one should remember that this condition has been proposed as that determining the limit between homogeneous and homeotropic alignment (29).

Weak anchoring would be found using surfaces having interaction with the L.C. weaker than the cohesion energy and still promoting a parallel alignment. However, these requirements could be contradictory.

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