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Alignment and alignment dynamics of nematic liquid crystals on Langmuir-Blodgett mono-layers

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Mono-layers of stearic and behenic acids, deposited with the Langmuir–Blodgett technique, were used as aligning films in nematic liquid crystal cells. During the filling process the liquid crystal adopts a deformed quasi-planar alignment with splay–bend deformation and preferred orientation along the filling direction. This state is metastable and transforms with time into a homeotropic state once the flow has ceased. The transition is accompanied by formation of disclination lines which nucleate at the edges of the cell. The lifetime of the metastable splay–bend state was found to depend on the cell thickness. On heating, an anchoring transition from quasi-homeotropic to degenerate tilted alignment in the form of circular domains takes place near the transition to the isotropic phase. The anchoring transition is reversible with a small hysteresis.

1. Introduction

Liquid crystal cells exhibiting uniform orientational alignment over large areas are required in most device applications. The usual techniques used to obtain a preferred orientation, or anchoring direction, rely on inducing physical or chemical interactions between a prepared substrate and the liquid crystal molecules [1]. Among them the Langmuir–Blodgett (LB) technique, which enables the deposition of organic aligning films with controlled molecular order and thickness and very high reproducibility [2, 3], is still in the research stage, but offers a high potential for future display alignment on an industrial scale.

When a substrate has been covered with a LB mono-layer, a possible aligning mechanism for a liquid crystal is that the molecules penetrate into the layer of aliphatic chains. They then adopt the orientation of these chains, which leads to homeotropic or conical anchoring, depending on the chain orientation [1].

In this work mono-layers of stearic (C18) and behenic (C22) acids were used as aligning layers in nematic liquid crystal (NLC) cells for obtaining a uniform homeotropic surface-induced orientation [4, 5]. The alignment was studied during the filling process and pursued during the relaxation to the equilibrium state. The temperature stability of this state was also investigated.

2. Experimental

2.1. *Film preparation*

Mono-layer formation was achieved by spreading a solution of stearic or behenic acid (see table 1) on the surface of ultrapure Milli-Q water in a LB trough (KSV 3000) held in a clean room environment to limit contamination of the trough by dust.

Table 1. Long chain fatty acids used in this experiment.

Common name	Structure	Abbreviation
Stearic	$C_{17}H_{35}COOH$	C18
Behenic	$C_{21}H_{43}COOH$	C22

The substrate used in the experiments was indium tin oxide (ITO) coated glass. Glass plates were cut to a size of $75 \times 20\,mm^2$ and pre-cleaned in an ultrasound bath filled with ultrapure water to eliminate the bigger dust particles and the residues from glass cutting. They were then cleaned during 8 min in an ultrasound bath filled with a mixture of five parts of H_2O, one part of NH_3, and one part of H_2O_2 at a temperature of 80°C. Finally they were rinsed in a three stage cascade with Milli-Q water and again rinsed and dried in a centrifuge. With this procedure we could eliminate both organic and inorganic contamination. The glass plates were stored in the clean room so that they could remain available in the cleaned state for at least two weeks.

The stearic and behenic acid solutions were made at a concentration of 1 mM in Merck chloroform. The sample material was spread on the water surface with a clean, all glass, Hamilton syringe. After a time lapse of *c.* 10 min to allow the solvent to evaporate, the mono-layer was compressed at a rate of approximately $0{\cdot}3 \times 10^{-3}\,nm^2\,s^{-1}$ molecule^{-1} until the required pressure was reached.

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The glass substrates were immersed in the sub-phase before spreading the mono-layer, and the transfer to the glass occurred during the extraction of the glass from the sub-phase at a controlled speed of $10\,\mathrm{mm\,min^{-1}}$, keeping the surface pressure constant.

2.2. *Cell fabrication and observations*

Sandwich cells were made with the ITO layers in the inner part (figure 1) and spaced with polyester films of various thickness supplied by Mylar. Care was taken not to touch, and thus contaminate, the inside surface of the cells.

The cells were capillary filled with MBBA (supplied by Aldrich) at room temperature. The observations on them were made using a microscope where the sample is inserted in a hot stage between crossed polarizers. Due to the birefringence of liquid crystals, the planar state, where the molecules lie parallel to the planes of the polarizers, appears very coloured and changes appearance as the sample is rotated. On the other hand, the homeotropic state, where the long axes of the liquid crystal molecules are oriented perpendicular to the planes of the polarizers, looks uniformly dark. The microscope was also equipped with a video-camera connected to a computer; it was possible to take pictures of the samples at regular time intervals and then record the evolution of the alignment state.

3. Results

3.1. *Isotherms*

In figure 2 the surface pressure versus molecular area isotherms for films of stearic acid (C18) and behenic acid (C22) are shown. Table 2 provides a summary of the three mono-layer phases observed in the isotherms of figure 2.

The deposition pressure for the LB films was chosen to $20\,\mathrm{mN\,m^{-1}}$. In this condition we have the liquid-condensed phase of the mono-layer for both compounds (see figure 2).

3.2. *Alignment*

The cells were capillary filled with MBBA at room temperature (where MBBA is in the nematic phase).

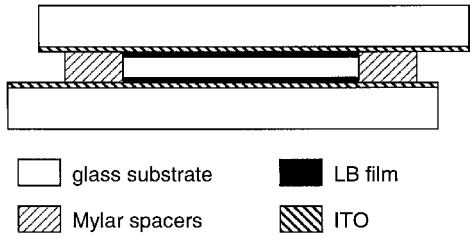


Figure 1. Cross-section of a cell. The ITO layer is in the inner part of the cell with the LB film on top of it. The proportions are symbolic.

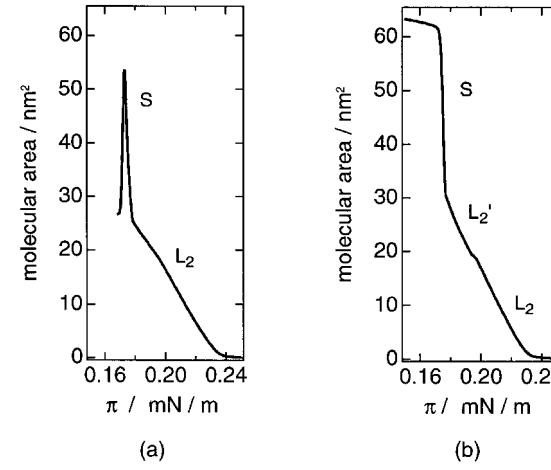


Figure 2. (*a*) Surface pressure versus area per molecule isotherm for stearic acid. The L_2, or liquid-condensed phase [2], and the S or solid phase can be distinguished. (*b*) Surface pressure versus area per molecule isotherm for behenic acid. In addition to the L_2 and the S phases, a slightly different liquid-condensed phase, the L_2' phase occurs. See table 2 for the phase characteristics.

Table 2. Condensed mono-layer phases for fatty acids (after Petty, [2]).

Phase	Name	Characteristics
L_2	Liquid-condensed	Slightly tilted molecular chains.
L_2'	Liquid-condensed	Tilted chains, but with tilt direction in excess of 45° relative to the L_2 phase; similar compressibility to the L_2 phase.
S	Solid	Upright molecules; less compressible than L_2 and L_2' phases; high collapse pressure.

During filling we have the alignment condition in which the orientation of the MBBA molecules is quasi-planar with a preferred alignment along the filling direction: the molecules in the centre of the cell are essentially parallel to the substrate and a splay–bend deformation in the NLC is induced by the presence of the aligning layer [6] [see figure 3 (*a*) and 3 (*b*)]. As soon as the flow stops, because the cell is completely filled with MBBA, domains of homeotropic alignment start to nucleate at the edges of the sample and continuously grow until the whole sample becomes homeotropic.

An example of how the homeotropic domains expand in the cell is given in figure 4. The line which divides the homeotropic domain from the quasi-planar domain is found to be a disclination line of strength $|S| = 1/2$. Such a disclination line should appear bright between crossed polarizers and dark between parallel polarizers [see figure 5]. A simple scheme of disclination lines of strength $|S| = 1/2$ is depicted in figure 6. Because of the

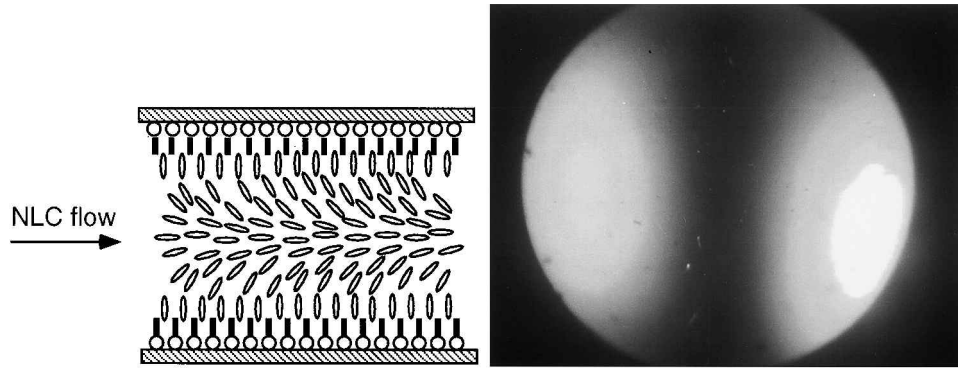


Figure 3. (*a*) During filling, the orientation of the LC molecules is quasi-planar (the molecules lie parallel to the glass substrate) with a preferred alignment along the filling direction. The molecules in the centre of the cell are essentially parallel to the substrate and a splay–bend deformation in the NLC is induced by the presence of the aligning layer [6]. (*b*) Conoscopic picture of a 22·3-μm-thick cell with aligning C18 mono-layer during the NLC filling. The picture shows that the NLC is oriented as depicted in (*a*) [7]: the molecules in the centre of the cell are aligned in the filling direction and a splay–bend structure is induced by the presence of the aligning LB films [8].

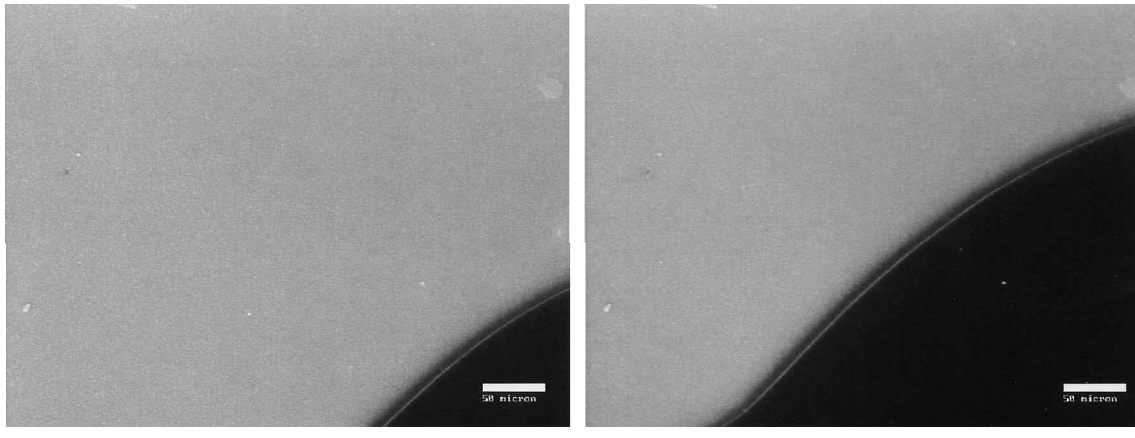


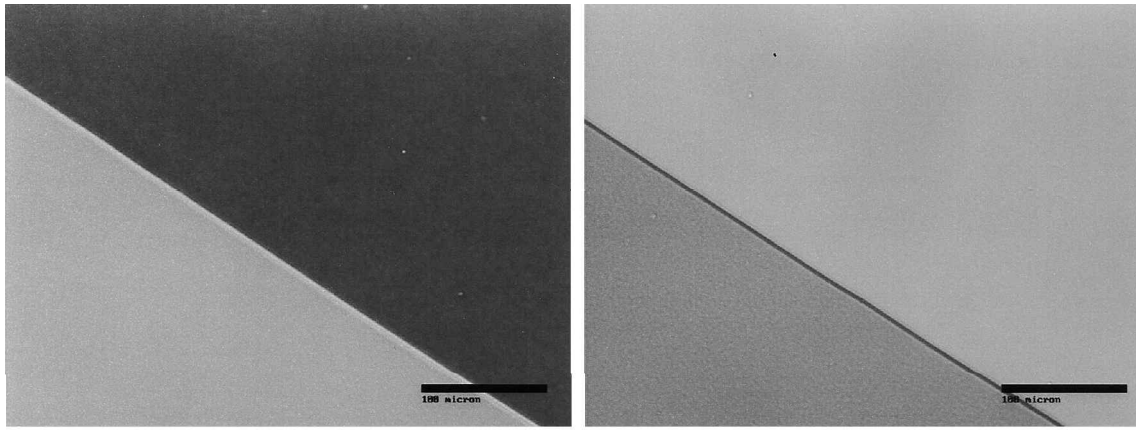
Figure 4. Cell between crossed polarizers; the LB aligning mono-layer is C18 and the thickness of the cell is 12·5 μm. The cell is completely filled with MBBA, the flow has ceased and the homeotropic domain (dark) expands into the quasi-planar domain (light). The two pictures were taken with a time interval of 30 s.

LB aligning layer, the defect moves into the quasi-planar area, the result being the expansion of the homeotropic domain.

A priori, we cannot know how much the fatty acid chains are affected by the filling flow. At a solid surface the flow velocity is zero, but here it may not be zero in the boundary layer of the chains. Nevertheless we have, in figure 3 (*a*), depicted these chains as being unaffected by the flow and shown them in their homeotropic equilibrium (static) condition. Under this hypothesis, the only driving mechanism behind the propagation of the splay–bend into homeotropic alignment is the elastic distortion in the liquid crystal.

The speed with which the homeotropic domains expand in the cells was measured by taking pictures at fixed time intervals for several cell thicknesses. The speed was calculated as the area covered by the front of the homeotropic domains in the time interval, divided by the length of the front and the time interval. The results are shown in figure 7. For both mono-layer materials, figure 7 shows that the speed of expansion of the homeotropic domains decreases as the cell thickness increases. For cells thinner than 12 μm the speed of expansion of the homeotropic domains is even larger than the actual speed of filling, so that no relaxation process can be observed.

Whereas the propagation speed of the disclination lines depends on the layer thickness, it does not depend on time. It is thus not a diffusive process. This conforms well with our previous hypothesis that the driving mechanism is the elastic relaxation of the splay–bend deformation in the liquid crystal, because the elastic torque



(a) (b)

Figure 5. (*a*) Cell between crossed polarizers: the aligning mono-layer is C18 and the cell thickness is 14·4 μm; the disclination line appears bright. (*b*) The same cell, a few seconds later, now between parallel polarizers: the disclination line appears dark.

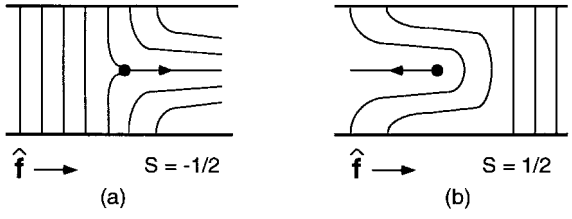


Figure 6. Schematic model of disclinations of strength $|S| = 1/2$; $\hat{\mathbf{f}}$ is the filling direction. The parallel vertical lines represent the homeotropically aligned area; the black circles represent the singularities which move into the quasi-planar splay–bend deformed domain. (*a*) An $S = -1/2$ singularity propagates along the filling direction. (*b*) An $S = 1/2$ singularity propagates against the filling direction. When two such lines meet, the singularities annihilate ($-1/2 + 1/2 = 0$), leaving a defect-free homeotropic domain.

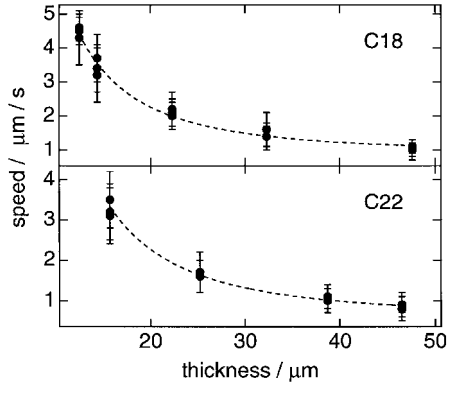


Figure 7. Speed of expansion of the homeotropic domains as a function of the cell thickness, for cells with C18 and C22 aligning layers. The dots are the experimental values and the dashed lines are fits to the function $a + bL^{-2}$, where a and b are constants.

will everywhere be the same behind the propagating front. Its speed will therefore be directly related to the speed of relaxation.

For a small disturbance of amplitude δn and wave vector q we may write the elastic free energy density as

$$\mathscr{F} = \frac{1}{2} K q^2 (\delta n)^2 \tag{1}$$

where K is the characteristic elastic constant. The elastic torque

$$\Gamma = -\frac{\partial \mathscr{F}}{\partial \delta n} = -Kq^2 \delta n \tag{2}$$

then gives the dynamic equation

$$\gamma \frac{\mathrm{d}\delta n}{\mathrm{d}t} + Kq^2 \delta n = 0 \tag{3}$$

where γ is the viscosity of the liquid crystal. The characteristic time of relaxation is then

$$\tau = \frac{\gamma}{Kq^2} \sim L^2 \tag{4}$$

where L is the cell thickness. In the present case this relaxation time towards the homeotropic state is proportional to the inverse speed with which the homeotropic domains expand in the quasi-planar domains, thus

$$v \sim L^{-2}. \tag{5}$$

The experimentally measured speed of expansion of the homeotropic domains were fitted to functional relations and (cf figure 7) a good agreement was found

with

$$v = a + bL^{-2}. \quad (6)$$

As $L \to \infty$, $v \to a$, and we may write

$$v = v_s + bL^{-2} \quad (7)$$

where v_s is a velocity of the order of $1\,\mu m\,s^{-1}$. As v_s is independent of L we interpret it as characteristic of the surface, coming from a rapid relaxation in the boundary layer of the chains, which propagates the homeotropic state into the liquid crystal bulk. We thus have to conclude that the chains are distorted by the filling flow, but rapidly and forcefully relax to their equilibrium (static) state. In other words, we believe that the LB film itself does have an active rôle in the dynamics of the alignment transition. Therefore figure 8 probably shows a more correct picture of the surface anchoring than does figure 3 (*a*) which corresponds to our original hypothesis.

The homeotropic alignment was studied by conoscopy and the conoscopic pictures of samples with the two aligning layers are shown in figure 9. As can be seen from the figure, a good homeotropic alignment was obtained with C18 as aligning layer and a much less good alignment with C22 as aligning layer. We believe that the reason for the different anchoring properties must be traced to the behaviour of C18 and C22 at the air–water interface, i.e. in the isotherms of figure 2. At the deposition pressure of $20\,mN\,m^{-1}$, C18 is in the liquid-condensed L_2 phase, while C22 is in the slightly more condensed liquid-condensed L_2' phase, where the molecules are strongly tilted with respect to the molecules in the L_2 phase. It is likely that this large tilt of the behenic acid chains causes a large pretilt of the NLC molecules instead of homeotropic alignment.

The alignment was found to be independent of the cell thickness, indicating the major rôle of the mono-layer material.

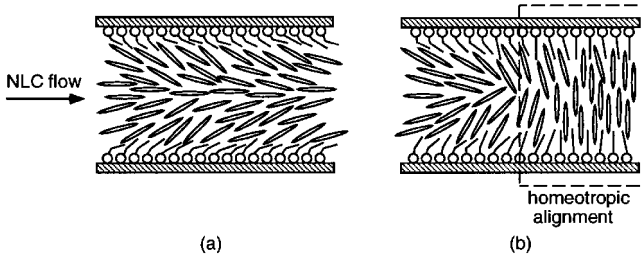


Figure 8. (*a*) During filling, the LB boundary layer seems to be strongly influenced with the chains aligning along the filling direction. (*b*) When the flow stops the LB film and the splay–bend deformed liquid crystal both contribute to the relaxation towards the homeotropic state.

3.3. *Anchoring transition*

On heating, we observed a first-order anchoring transition [4] in a very narrow temperature range, just below the clearing point. At the transition a set of bright circular domains with dark crosses appears in the sample; at constant temperature, they grow and coalesce, forming larger domains. The appearance of these domains between crossed polarizers is consistent with a degenerated tilted orientation of the NLC molecules, or conical anchoring, also expected in the case of LB aligning films [1].

On increasing the temperature, the transition to the isotropic phase takes place inside the domains [figures 10 (*a*) and 10 (*b*)]. On cooling from the isotropic phase the bright domains appear again and the transition

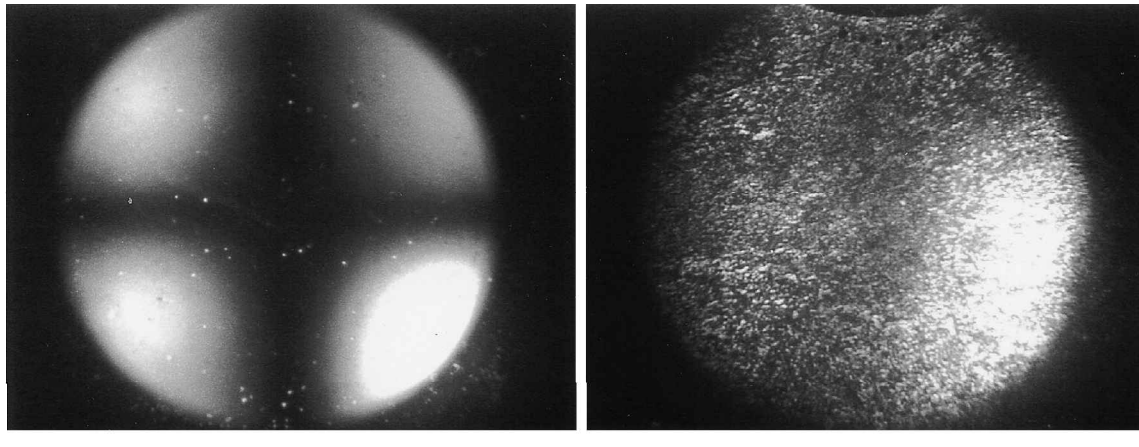


Figure 9. (*a*) Conoscopic picture of a 14·4-μm-thick cell with C18 as aligning layer: a very good homeotropic alignment is achieved. (*b*) Conoscopic picture of a 15·7-μm-thick cell with C22 as aligning layer: the alignment is not homeotropic and not well defined. For both mono-layer materials the alignment is found to be independent of cell thickness.

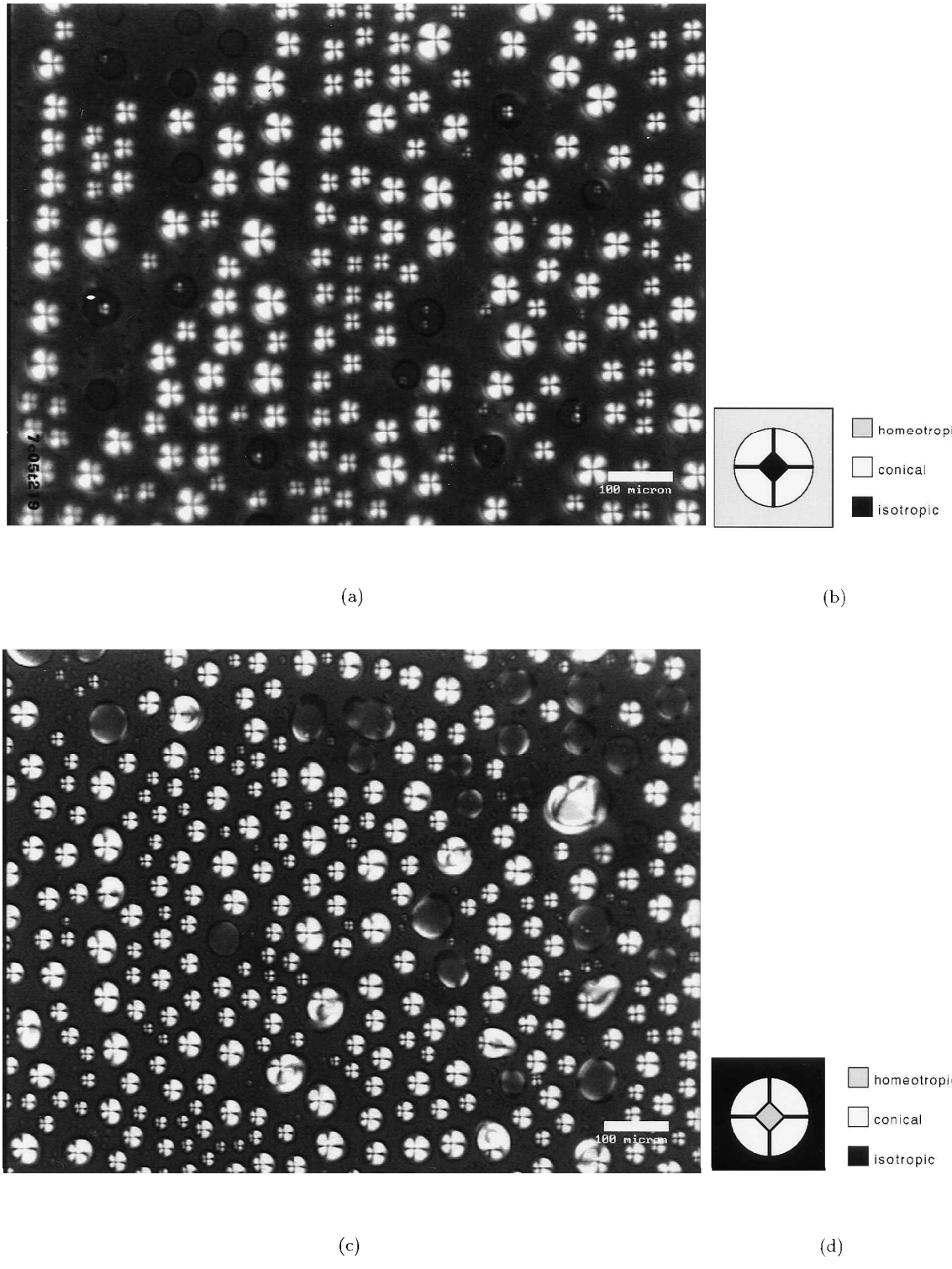


Figure 10. (*a*) Nematic to isotropic phase transition in a cell with C18 as aligning layer; the dark grey background is the homeotropic phase. In the circular domains the alignment is conical; the isotropic phase appears inside the domains. (*b*) Scheme of the homeotropic to isotropic phase transition. (*c*) Isotropic to nematic phase transition in the same cell; now the dark background is the isotropic phase and in the circular domains the alignment is again conical. The homeotropic state appears inside the domains. (*d*) Scheme of the isotropic to homeotropic phase transition.

to the nematic phase takes place inside the domains [figures 10(*c*) and 10(*d*)].

Following Safran *et al.* [9], we think that the surfactant's molecules are arranged in soliton–antisoliton pairs randomly distributed over the substrate area. Depending on the length of the tails and on the temperature, those structures can be large enough to prevent the uniform homeotropic alignment, which may be the case in the C22 mono-layer. If the soliton–antisoliton pairs are not too large, they can give a uniform homeotropic alignment in the bulk. However, they are the germs of the conical structures appearing at the anchoring transition.

4. Conclusions

The surface induced homeotropic alignment in NLC cells by LB mono-layers of stearic and behenic acids has been investigated. Stearic acid was found to be very good for aligning NLC in the homeotropic state, whereas behenic acid does not give a well defined alignment.

A relaxation process from the flow induced quasi-planar orientation to the surface induced homeotropic orientation has been observed. It takes place once the cell is filled with the liquid crystal such that there is no further material flow. It starts from the edges of the cell in the form of expanding homeotropic domains. The disclination lines dividing the homeotropic domains from the quasi-planar domains have strength $|S| = 1/2$ and move at a speed dependent on the thickness of the cell. The speed, which is also the speed with which the homeotropic domains expand in the cell, was found to decrease as the cell thickness increased, in accordance with a single model involving both the elastic relaxation of the liquid crystal splay–bend deformation and the relaxation of the deformed LB chains.

Further studies of this relaxation process could be useful to understand the anchoring mechanism and in estimating anchoring energies. In the future, computational simulations may play an important rôle in giving answers to several remaining questions, but more experiments are also needed to formulate the right models.

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