

## Multistable alignment in free suspended nematic liquid crystal films

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Two different types of orientation were observed in free suspended nematic liquid crystal films. The alignment was either homeotropic or planar, depending on the time during which the film was cooling from the isotropic state to the liquid crystal one. It was shown that nucleation of defects makes planar orientation preferable. [S1063-651X(99)50810-6]

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### I. INTRODUCTION

All the liquid crystal applications are based on the simple fact that liquid crystals can be easily aligned by a proper surface treatment of the surface of the material in contact with the liquid crystal. The preferred direction imposed by the surface is transmitted into the bulk because of long range orientational order in liquid crystals. The structure of such a system is a result of the competition of intrinsic ordering on one hand and surface induced effects on the other. Much work has been done on orientation of liquid crystal on a solid substrate; see, for example, reviews [1,2]. The orientation that is imposed onto a liquid crystal by an isotropic surface is studied much less. Despite the seemed simplification, since only the polar angles of the director orientation are fixed at interfaces and the molecular interactions do not fix the azimuthal orientation, this object is still far from being understood and is an attractive matter for consideration. The simplest example of an interface between a liquid crystal and isotropic matter is a free surface of liquid crystal. The observed phenomena at an air-nematic liquid crystal interface

can be summarized as follows [3–9]: (i) the easy director orientation of 4-*n*-pentyl-4'-cyanobiphenyl (5CB) nematic liquid crystal is orthogonal at the free surface [9]; (ii) the free suspended liquid crystal films of 4-methoxybenzylidene-4'-butylaniline (MBBA) exhibit the both planar or orthogonal orientation depending on the thickness of the film as well as on the temperature [7,8]. We have investigated the thing (the thickness was varied between 4-8  $\mu\text{m}$ ) free suspended nematic liquid crystal films of 5CB. We observed both the homeotropic and planar orientations. The type of the obtained structure was the result of the temperature gradient during the cooling from the isotropic state to the liquid crystal state. For the slow cooling the liquid crystal always had homeotropic orientation, and for the fast cooling the resulting structure is planar.

### II. EXPERIMENT

To suspend liquid crystal films, copper foil 10  $\mu\text{m}$  thick was used with a square hole of 450  $\mu\text{m}$  and a distance be-

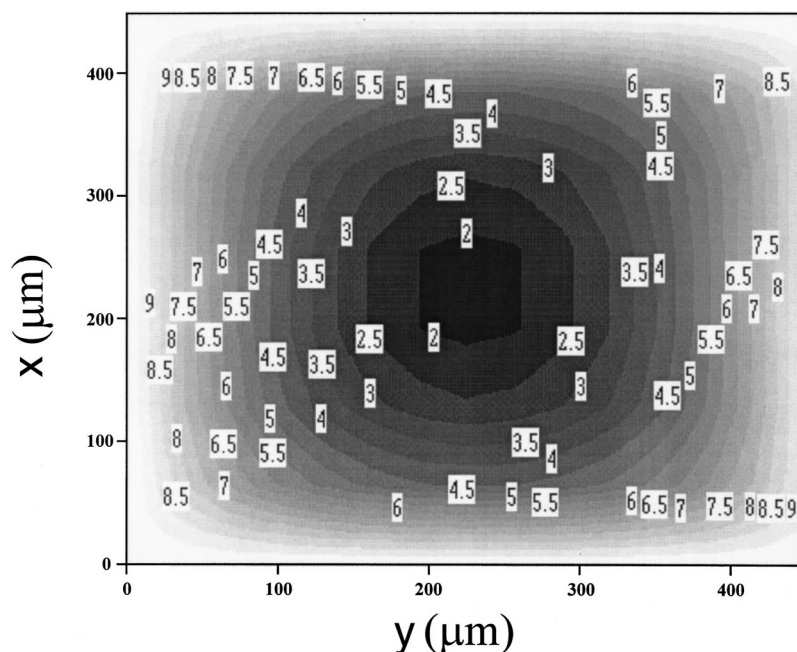


FIG. 1. Typical profile of the free suspended nematic liquid crystal film. The thickness of the film is marked directly on the picture.

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tween neighboring holes of  $50 \mu\text{m}$ . The 5% solution of liquid crystal 5CB in hexane was dropped on the foil. When the hexane evaporated, the liquid crystal formed uniform films within the holes. After this, the foil with liquid crystal films was placed in the microscope heating stage (HS1-i, Instec, Inc.). The temperature was changed with the accuracy of 0.03 K. The thickness of the liquid crystal films was determined by the interference microscopy method.

### III. RESULT AND DISCUSSION

The orientation of molecules in freshly prepared free suspended liquid crystal films was homeotropic. The typical profile of the films is shown in Fig. 1. The nematic film profile does not change during the heating to the isotropic state and cooling back while the orientation of liquid crystal suffers the drastic change. The velocity of cooling effected the resulting structure. Thus, if the temperature is going from  $50^\circ\text{C}$  down to the temperature that corresponds to the nematic to isotropic phase transition (in our case this is  $34.6^\circ\text{C}$ ), for 100 s, one can observe homeotropic orientation in each hole [see Fig. 2(a)]. Decreasing the cooling time to 40 s, some holes demonstrated planar orientation of the liquid crystal; see Fig. 2(b). Note that planar orientation forms occasionally; for each thermal cycle planar orientation appears in a different hole. Figure 2(c) shows the structure of liquid crystal films for 30 s cooling time. In this case planar orientation becomes dominated. Additional heating or cooling within the nematic phase does not influence the already obtained structure. To understand this phenomenon, let us consider the nematic layer with the profile shown in Fig. 1 in the right-hand coordinate system where the axis  $\vec{z}$  coincides with the normal to the layer. The behavior of the nematic liquid crystal layer is described by the total free energy [10]

$$F_d = \frac{1}{2} \int d\vec{r} \{ K_{11} (\vec{\nabla} \vec{n})^2 + K_{22} (\vec{n} \vec{\nabla} \times \vec{n})^2 + K_{33} (\vec{n} \times \vec{\nabla} \times \vec{n})^2 \}, \quad (1)$$

where  $K_{11}$ ,  $K_{22}$ , and  $K_{33}$  are the elastic constants, and  $\vec{n}$  is the director. For a general case one can define the director in the form  $\vec{n} = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$ , where  $\theta = \theta(z)$  is the angle that describes the tilt of the director along axis, and  $\varphi = \varphi(z)$  is the azimuthal angle in the plane of the cell. Taking the  $\partial \theta / \partial z = \theta(d) - \theta(0) / d$ , for the homeotropic orientation of liquid crystal one can obtain the free energy per unit area as follows:

$$F_H = K_{33} \left( \frac{\theta_0}{d} \right)^2 d + W \theta_0^2, \quad (2)$$

where  $d$  is the thickness of the cell,  $W$  is the anchoring coefficient for nematic-air interface, and  $\theta_0$  is the angle that describe the inclination of nematic layer [11]. For the planar orientation one can get

$$F_P = K_{11} \left( \frac{\theta_0}{d} \right)^2 d + W \sin^2 \left( \frac{\pi}{2} - \theta_0 \right). \quad (3)$$

Taking into account  $K_{11} = 6.2 \times 10^{-12} \text{N}$ ,  $K_{33} = 8.25 \times 10^{-12} \text{N}$  [12],  $W = 4 \times 10^{-6} \text{J/m}^2$  [9],  $d = 8 \mu\text{m}$ , and  $\theta_0$

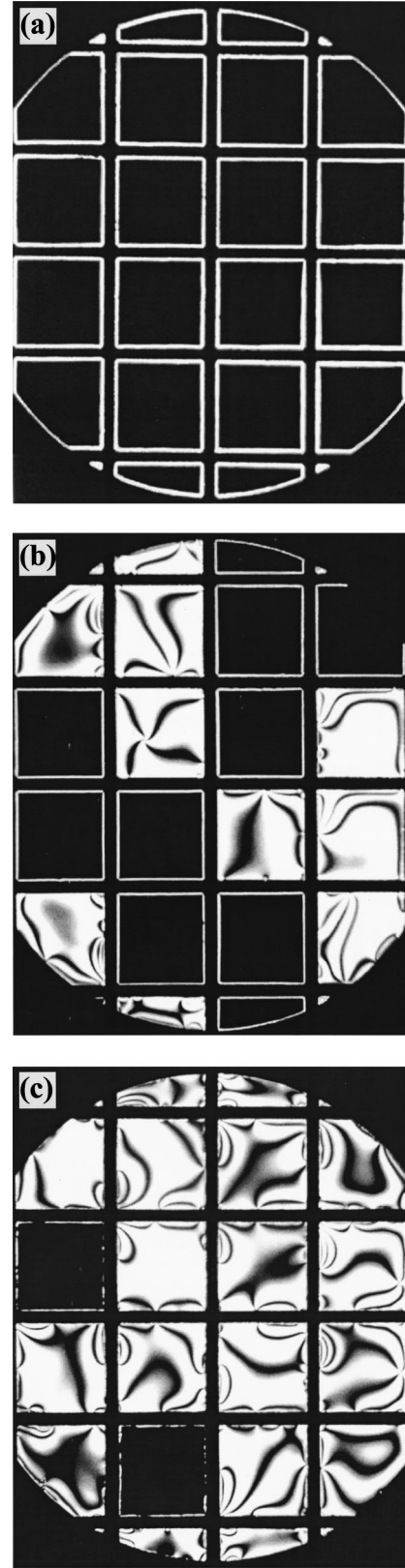


FIG. 2. Structure of the free suspended nematic liquid crystal film obtained by cooling from the isotropic phase; (a) cooling time is 100 s, (b) cooling time is 40 s, (c) cooling time is 30 s.

$= 0.02 \text{ rad}$  (see Fig. 1), we can find from Eqs. (2) and (3) that  $F_H = 12.25 \times 10^{-10} \text{J/m}^2$ ,  $F_P = 4 \times 10^{-6} \text{J/m}^2$ . Obviously,  $F_P \gg F_H$ , the homeotropic alignment will be realized.

For the sharp cooling, liquid crystal film will create a

number of crystallization centers. Thus, one can expect the existence of domain walls for  $d < b$  or surface lines for  $d > b$  [13], where  $b = K/2W$  is the extrapolation length. The total energy for the wall is equal to  $E_W = \pi \sqrt{2dK_{22}W} = 4.3 \times 10^{-5} \text{ J/m}^2$  [13], where  $K_{22} = 3 \times 10^{-12} \text{ N}$  [14]. The total energy for the surface line is equal to  $E_L = 2\pi K_{22} = 1.9 \times 10^{-5} \text{ J/m}^2$  [13]. In this case to realize homeotropic alignment, the liquid crystal layer should overcome the state that has higher free energy than planar state. Because of this, the planar alignment is energetically preferable,

$$F_W > F_L > F_P > F_H. \quad (4)$$

Truly speaking, the orientation of liquid crystal layer showed in Fig. 2(c) is not exactly the planar one. Moreover,

this orientation is the most probably tilted or double hybrid. But either tilted or double hybrid orientation has a lower free energy than we consider for planar alignment. In this case inequality (4) will be automatically fulfilled.

To conclude, it is shown that specific orientation behavior of free suspended nematic liquid crystal films is governed by elastic forces.

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