CONFINED LIQUID CRYSTALS - POLYMER DISPERSED LIQUID CRYSTAL FILMS

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The paper presents an interesting discussion on the anchoring energy of liquid crystals at a solid interface, considering the anisotropic part of the free energy proposed by Rapini. Simulations of the anchoring energy when strain is applied suggestively show the evolution of the deformations of the anchoring energy.

A polymer dispersed liquid crystal film was experimentally obtained using a thermotropic nematic LC and polymethyl methacrylate by the solvent induced phase separation method. Observations under polarized optical microscopy showed encapsulated droplets, with dimensions in the micrometer range, with a well defined small twist radial configuration. The calculated anchoring energy density confirms the strong anchoring at the polymeric walls.

Keywords: liquid crystal, anchoring energy, polymer dispersed liquid crystal

1. Introduction

The liquid crystal (LC) – substrate interface has been thoroughly studied [1,2] due to its importance and specific characteristics. When confined [3-7], the structure and behaviour of LCs are different from the bulk. In many of their applications LCs are confined: thin LC layers [2], LC droplets encapsulated in polymers [1, 8-11], LC channels in solid or soft solid matrices [1,10,11], the latter two forming polymer liquid crystal (PDLC) films and devices.

PDLC films are formed by LC droplets embedded in a polymeric matrix [12-14]. The internal structure of the nematic in the droplet, its dimensions, interface phenomena, are important factors determining the reorientation of the LC molecules when an external electric field is applied across the film. For PDLCs with LCs' positive dielectric anisotropy, $\Delta\varepsilon > 0$, when applying an alternative voltage across the film, the LC molecules reorient in the direction of the electric field, the refraction index of the LC will equal the refraction index of the polymer and the film will become transparent.

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2. LC-solid interface

Figure 1 presents the equilibrium alignment of the LC director, $\vec{n}_0(\theta_0,\phi_0)$, called the easy axis. At the free surface of the nematic the easy direction settles spontaneously and at the nematic-solid interface it is determined by the treatment of the surface. The alignment can be homeotropic for $\theta_0 = 0$, planar $\theta_0 = \frac{\pi}{2}$ or tilted for $0 < \theta_0 < \frac{\pi}{2}$. The surface free energy of the nematic $F^S(\theta,\phi)$ is minimum for $\theta = \theta_0$ and $\phi = \phi_0$. It is formed by an isotropic and an anisotropic part, which shows the energy needed to deflect the director from the easy direction to which it is anchored and it is named anchoring energy.

Firstly, let us consider a nematic layer between two plane surfaces, where the director is deviated only in the *xz* plane through the angle ϕ, and $\theta = \pi/2$.

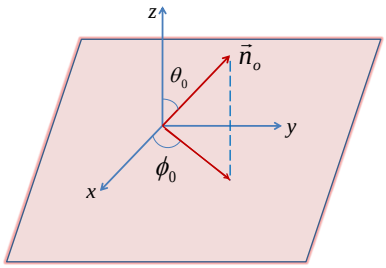


Fig. 1. Equilibrium position of the LC director $\vec{n}_0$; ϕ_0 -azimuthal angle, θ_0 - zenithal angle.

The free energy $F(\phi)$ of the LC will be [1]:

$$F(\phi) = \int g\left(\phi, \frac{\partial\phi}{\partial z}\right)dz + F_1^S(\phi) + F_2^S(\phi) \tag{1}$$

where $g\left(\phi, \frac{\partial\phi}{\partial z}\right)$ is the Frank energy density. The equilibrium alignment of the director in the space between the solid surfaces might be found by minimizing the integral equation (1), which requires knowledge of the functions F_1^S and F_2^S. Rapini [2] energy, F^S is usually used, which has the form:

$$F^S = F_{iso}^S + \frac{1}{2}W\sin^2(\phi - \phi_0) \tag{2}$$

where F^S is the surface free energy of the LC, F_{iso}^S is the isotropic free energy and the term $\frac{1}{2}W\sin^2(\phi - \phi_0)$ corresponds to the anisotropic part of the free

energy, with W being an anchoring energy and $(\phi - \phi_0)$ is an angle of director deflection from the equilibrium angle ϕ_0. In the case of a LC confined in solid matrices, both angles are changed and two Rapini energies should be introduced. For fixed zenithal angle θ_0, we define the azimuthal energy as:

$$F_a^{\phi}(\theta) = \frac{1}{2} W_{\phi}(\theta_0) \sin^2(\phi - \phi_0) \tag{3}$$

For fixed azimuthal angle, ϕ_0, the zenithal (polar) energy is defined as:

$$F_a^{\theta}(\phi) = \frac{1}{2} W_{\theta}(\phi_0) \sin^2(\theta - \theta_0) \tag{4}$$

The total surface anchoring energy is

$$F_s = \frac{1}{2} W_{\theta 0} \sin^2(\theta - \theta_0) + \frac{1}{2} W_{\phi 0} \sin^2(\phi - \phi_0) \tag{5}$$

where θ_0 and ϕ_0 are fixed zenithal and azimuthal angles of the easy axis.

3. Experimental

Sample preparation

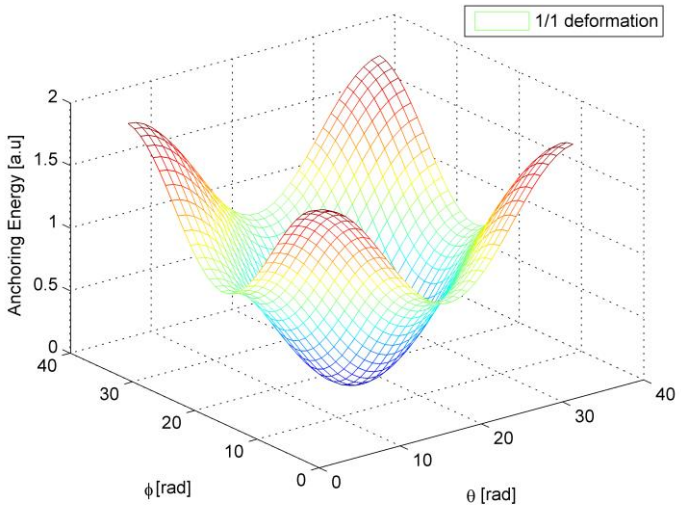
We have prepared PDLC by the SIPS method, using the nematic W 765 (MUT, Poland), ordinary refractive index $n_O = 1.51$) and the polymethyl methacrylate (PMMA, refractive index $n_P = 1.49$), in a ratio of 40/60 (LC/PMMA) w.w. by the solvent induced phase separation method. The LC exhibits a nematic to isotropic transition at 60 ºC, and positive dielectric anisotropy $\Delta\varepsilon>0$. Chloroform was poured in the mixture, in a proportion of 1:9 ((E7+PMMA): chloroform). The mixture was thoroughly homogenized by magnetic stirring for about one hour. A thin film was deposited on an ITO covered glass plate and the solvent was evaporated at room temperature. The sample was placed in a heated oven at 110 ºC and left for one hour and then cooled down to room temperature (approx. cooling rate 0.5 ºC/min).

4. Results and discussions

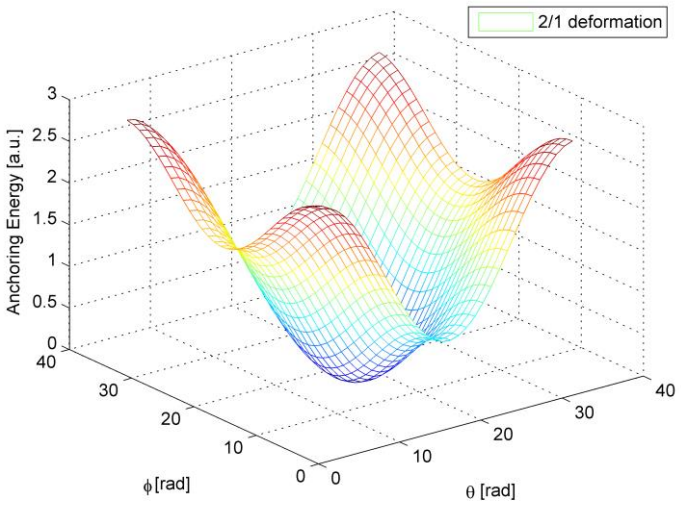
4.1 Numerical simulation

In Fig. 2 are represented the ratio of the azimuthal and zenithal anchoring energies: fig.2a, $\frac{W_{\theta 0}}{W_{\phi 0}} = 1$: equal azimuthal and zenithal (polar) energies and

fig.2b, $\frac{W_{\theta 0}}{W_{\phi 0}} = 2$, the zenithal energy is in excess. In other words, there is a strain applied in the angular directions of ratio $\frac{W_{\theta 0}}{W_{\phi 0}}$.

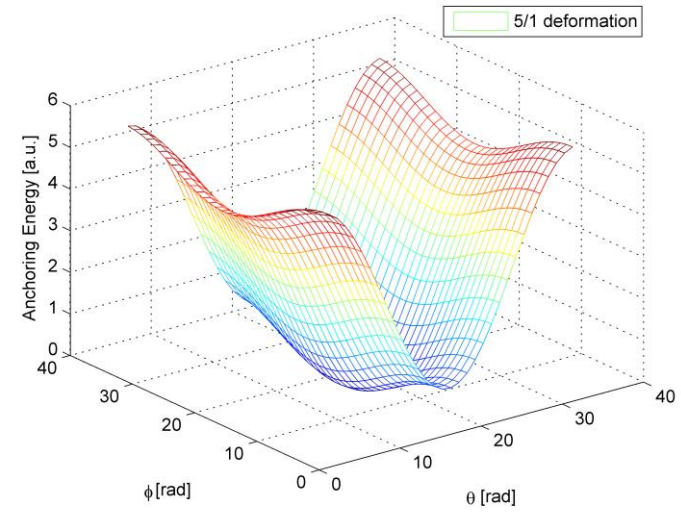


a)

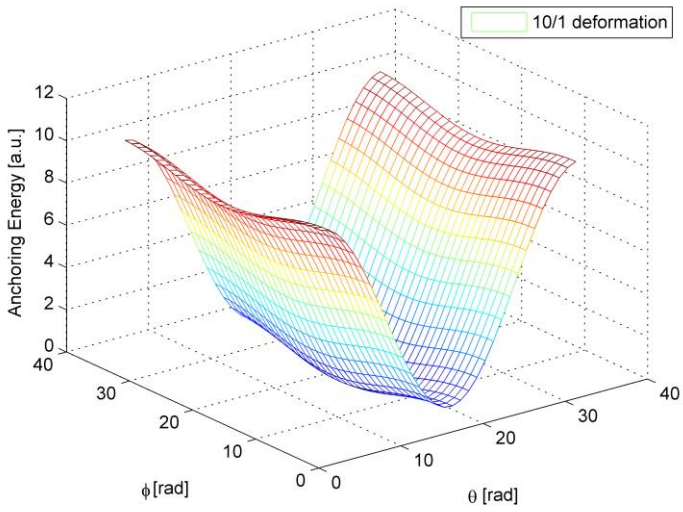


b)

Fig. 2. Anchoring energy when strain is applied on the angular directions at a) 1/1 ratio; b) 2/1 ratio.



a)



b)

Fig. 3. Anchoring energy when strain is applied on the angular directions at a) 5/1 ratio; b) 10/1 ratio.

In Fig. 2a, a minimum of the anchoring energy is noticed in the center of the (θ,ϕ) plane; at the increase of the deformation ratio $\frac{W_{\theta 0}}{W_{\phi 0}}$ (figs. 2b, 3a, 3b) it evolves towards a saddle-like form (fig. 3b).

4.2 POM observation: The case of a nematic droplet

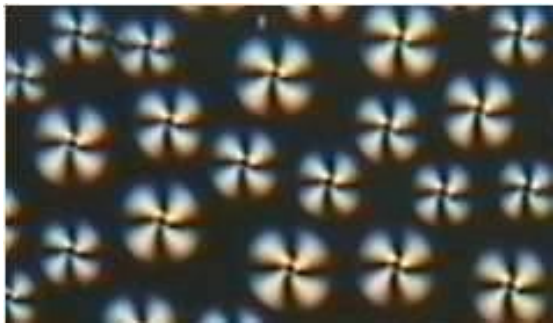


Fig. 4 POM image of W 765/PMMA film.

In Fig. 4 is presented the POM image of the obtained PDLC film and in Fig. 5 the schematic representation of the LC director patterns in radial and twisted radial droplets. By comparing Figs. 4 and 5 we draw the conclusion that the obtained droplets have a radial structure with a small twist in the center (Fig. 5b). The LC directors are perpendicular to the polymer surface.

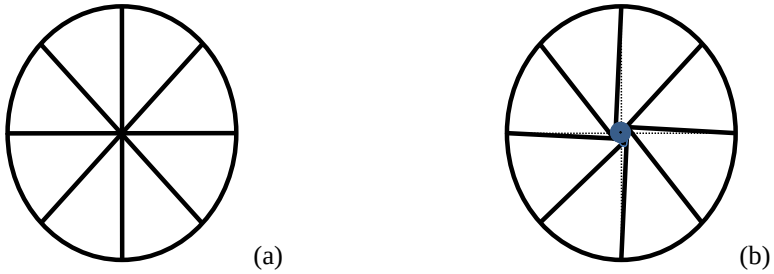


Fig. 5: Schematic representation of LC director patterns in a droplet: radial structure (a) and twisted radial (b).

Anchoring energy in a LC droplet

The anchoring energy $E_{anchoring}$ for a droplet scales as the anchoring energy density ($\frac{1}{2} w \cdot \sin^2 \theta$) times the area of the sphere of radius R [1]:

$$E_{anchoring} = \left(\frac{1}{2} w \cdot \sin^2 \theta \right) \left(4\pi R^2 \right) \tag{6}$$

In order to affect the LC droplet structure, we compare this energy to the elastic free energy:

$$E_{elastic} = \left(\frac{1}{2}\frac{k}{R^2}\right)\left(\frac{4}{3}\pi R^3\right) \tag{7}$$

where k is the elastic constant, of the order of $10^{-11} J/m$.
Equalizing relations (5) and (6), results the anchoring energy density as:

$$w = \frac{k}{3R\sin^2\theta} \tag{8}$$

The obtained droplets are polydispersed and typically they have the radius of the micrometer order ($(2 \div 4)\mu m$). From (8), the resulted "anchoring coefficient" w is of the order of $10^{-5} J/m^2$, being compatible with the polymers' anchoring energy densities. The surface energy density is considered to be strong in the $10^{-4} \div 10^{-6} J/m^2$ range and weak when smaller. As the POM image shows, the obtained PDLC film has well defined radial structure, suggesting a strong anchoring at the polymeric walls.

6. Conclusions

The paper presents an interesting discussion on the anchoring energy of LCs at a solid interface, considering the anisotropic part of the free energy proposed by Rapini. Simulations of the anchoring energy when strain is applied suggestively shows the deformations of the anchoring energy.

A PDLC film was experimentally obtained using a thermotropic nematic LC (W765) and the PMMA by the solvent induced phase separation method. Observations under POM showed encapsulated droplets, with dimensions in the micrometer range, with a well defined small twist radial configuration. The calculated anchoring energy density confirms the strong anchoring at the polymeric walls.

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