

## Ordered Droplet Structures at the Liquid Crystal Surface and Elastic-Capillary Colloidal Interactions

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We demonstrate a variety of ordered patterns, including hexagonal structures and chains, formed by

glycerol droplets at the surface of a liquid crystal film. The droplets are formed by cooling the sample to  $T < T_{LC}$  for 10 min, to facilitate diffusion of the glycerol molecules into the 5CB layer which is in the isotropic phase above  $\approx 35^\circ\text{C}$ . When the sample is cooled down, solubility decreases and one observes appearance and growth of glycerol droplets. The technique produces droplets of a constant radius  $R$  determined by the cooling rate and the number of thermal cyclings. The thickness of the LC film is controlled in the range  $h = (3-100)\ \mu\text{m}$ . The 5CB film is in the hybrid aligned state: the director  $\mathbf{n}$

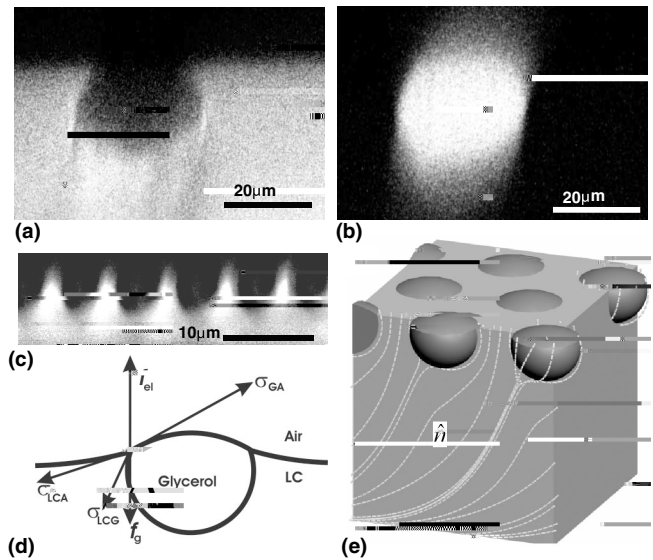


FIG. 1. Two-channel FCPM textures of the vertical cross section of the LC film: (a),(b) a single glycerol droplet at the LC-air interface; (c) a row of droplets that is a part of a hexagonal pattern at the LC-air interface; (d) scheme of forces and interfacial tension vectors at the LC-air interface with a strongly exaggerated meniscus slope; (e) 3D director field in the LC layer. The LC layer (glycerol droplet) is manifested by the high (low) intensity of fluorescent light in parts (a), (c); the contrast is opposite in (b).

is parallel to the LC-glycerol interface at the bottom and perpendicular to the LC-air interface at the top.

In order to determine the location of droplets, we use the fluorescence confocal polarizing microscopy (FCPM) [23]. Two different dyes with separated absorption and fluorescence bands, fluorescein and Nile red (Aldrich), were added (0.01 . %) to tag glycerol and LC, respectively [23]; they did not change the appearance of patterns. The FCPM textures of vertical cross sections, Fig. 1(a)–1(c), unambiguously demonstrate that the glycerol droplets are trapped at the LC-air interface. For a better clarity, the images in Fig. 1(a) and 1(b) are taken for a large drop; smaller drops are also located at the interface, Fig. 1(c).

A 4–6 h relaxation at room temperature results in 2D

length;  $\Pi \approx K/h^2$  is the elastic disjoining pressure for the hybrid aligned film [22];  $K \sim 10^{-11} N$  is the average nematic elastic constant; in all cases of interest to us,  $\lambda \gg r_{eq}$ , as  $\lambda \approx 2$  when  $h \rightarrow \infty$  and  $\lambda \approx 0.5$  when  $h \sim 5 \mu$ ; finally,  $A$  is the Hamaker constant of the order of  $10^{-19}$  J or smaller [22].

Attraction of droplets at the nematic surface (and absence of attraction and ordering when 5CB is in the isotropic state) can be explained by the coupling of orientational elasticity and capillarity. The elastic distortions caused by the submerged part of the particle give rise to a vertically resolved force  $f_{el}$  that shifts the LC-air interface upward or downward, depending on the particle properties, to reduce the elastic energy of the LC host;  $f_{el}$  is balanced by surface tension. Nonflat interface causes long-range attraction of particles. As the first approximation, we divide the total interaction potential  $U(r)$  into two parts,  $U_{elc}(r)$  describing the elastic-capillary coupling and  $U_{elb}(r)$  describing the “pure bulk” elastic interactions.

To estimate the orders of magnitude, we use the idea that  $f_{el}$  is related to the nonvanishing surface anchoring of  $\mathbf{n}(r)$  at the LC-particle interface:

$$f_{el} = \frac{\partial}{\partial z} E_{el}(z) \sim \frac{\partial}{\partial z} \oint_{\Omega(z)}$$

In the thin films,  $\mathbf{n}$  becomes progressively horizontal at the LC-air interface as the anchoring coefficient  $W_{air}$  there is smaller than  $W$  [26]. When  $h$  decreases to  $2R$  and  $K/W_{air}$ , the boojum shifts to the side, Fig. 3(b), giving rise to the in-plane elastic dipole component,  $p_x$

$\alpha$