

## Dynamics of molecular exchange between aligning adsorbed film of liquid crystal and the bulk

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The liquid crystal (LC) originally filled in thin cells is replaced by a different LC having a drastically different pretilt angle. The mechanism of desorption/adsorption of LC molecules from/on the adsorbed LC film at the substrate changes the composition of the adsorbed layer and thus the pretilt angle. The time dependence of molecular pretilt angle at solid surfaces of homogeneously aligned LC cells is measured. The characteristic molecular exchange time depends on the coefficients of desorption of the first LC. The results presented here provide an important insight into the molecular exchange between solid surface and bulk fluid. © 2008 American Institute of Physics.

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Anchoring properties of liquid crystals (LCs) are determined by the anisotropy of the alignment layer<sup>1</sup> and its interaction with the LC bulk. Regardless of the aligning material used, a layer of LC molecules is adsorbed on to the aligning surface and contributes to the anchoring of bulk LC. The anchoring energy  $W$ , due to the adsorbed molecules, is of the order of  $10^{-5}$ – $10^{-7}$  J m<sup>-2</sup>. It is comparable to the anchoring energy of LCs on rubbed polyimide and photoaligning layers.<sup>2,3</sup> Therefore, the contribution of the adsorbed LC film is important, and in some cases, it solely determines the alignment of LC on the boundary surface as well as the alignment memory effect,<sup>4,5</sup> light-induced anchoring,<sup>3</sup> and magnetically induced alignment.<sup>6,7</sup> However, this phenomenon remains poorly understood. Ouchi *et al.* and Vetter *et al.*<sup>8,9</sup> explained the observed weakening of magnetically induced alignment as being due to increased rotational diffusion of the adsorbed LC molecules upon heating. Recently, we reported<sup>10</sup> that the anchoring energy of an adsorbed layer in a magnetically aligned cell decreased after thermal treatment. We established the dependence of this decrease on the changes in the angular distribution of the adsorbed molecules caused by molecular exchange between the adsorbed layer and the LC bulk, i.e., adsorption (desorption) of bulk LC molecules on to (from) the adsorbed alignment layer. The experimentally measured temperature dependence of the anchoring energy allowed us to estimate the activation barrier,  $\Delta E \approx 2.16$  eV, for the process between LC pentylcyanobiphenyle (5CB) on indium tin oxide (ITO) surface and the probability of desorption,  $A_- \approx 6 \times 10^{-6}$  s<sup>-1</sup>, of these molecules at room temperature.

Here, we report experimental proof of intensive molecular exchange between the adsorbed alignment film and the LC bulk. The experiment monitors the dynamics of the pretilt angle of *one* LC (LC-1) on a layer of the adsorbed molecules of *another* LC (LC-2). The pretilt angles,  $\theta_{ii}$  ( $i=1,2$ ), of each LC on a layer of adsorbed molecules of the same LC are different. (Here, the first subscript denotes the

“bulk” LC molecules and the second subscript denotes LC molecules adsorbed on the aligning surface.) Therefore, in cells in which aligning surfaces are formed via adsorption of LC-1 molecules and which are filled with LC-2, the molecular exchange between the adsorbed layer and the bulk should result in a gradual change of the pretilt angle. Desorption of LC-1 molecules and their dispersion into the bulk of LC-2 followed by reverse adsorption of LC-2 molecules eventually results in the replacement of the adsorbed layer of LC-1 by the layer of LC-2 and, correspondingly, a change in the pretilt angle from  $\theta_{1,2}$  (of LC-1 molecules on a layer of LC-2) to  $\theta_{2,2}$ . To the best of our knowledge, the experiments described here, with an *in situ* exchange of molecules between a solid surface and bulk fluid, have never been reported. This experiment became possible due to long-range orientational interactions in the nematic phase, which render this method highly sensitive to the alignment of the LC and anchoring conditions.

To clearly prove intensive molecular exchange between aligning surface and LC bulk, we needed to find an aligning layer that provided essential difference in the pretilt for two different LCs. Seo observed a large difference in the pretilt angle of 5CB and ZLI-4792 on a fluorinated polyimide layer.<sup>11</sup> Therefore, we chose the same LCs but the fluorinated polyimide poly(2,6-piperazinedione) (PPZD) based on 5-perfluorooctyl-1,3-phenylenediamine as the aligning layer. This polyimide was synthesized according to example 8 in Ref. 12 where a high pretilt for ZLI-4792 ( $>20^\circ$ ) was reported. This polyimide is quite different from the one in Seo’s paper, mainly in the position of the fluorinated branch on the polyimide molecule, which results in a different pretilt angle for 5CB and ZLI-4792.

We used planar cells made from ITO coated glass substrates. Inner surfaces of the glass substrates were covered with alignment layers of polyimide PPZD. The polyimide coated surfaces were rubbed and then assembled in to a cell in antiparallel configuration which provided homogeneous alignment of both the LCs. The thickness of the cell,  $L = 50$   $\mu\text{m}$ , was controlled with the help of internal polymer

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