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## Thin films of nematic liquid crystal on liquid substrate. Bulk and surface structures, surface and line tensions

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### Introduction

The surface tension  $\gamma$  of liquids is the result of the excess values of local free energy at the surface originating in the excess values of degree of order: density and orientation of molecules near the interface (1). The orientation of surface molecules of L.C can be determined (2). This orientation is determined by the minimum of  $\gamma(\theta)$ , where  $\theta$  is the angle of the molecular axis with the normal, for macroscopic films or drops. If  $\theta$  can be modified,  $\gamma(\theta)$  can be deduced.

The line tension  $\varkappa$  is the result of the excess free energies of molecules in the contact line between three phases, a heterogeneous intermediate region. Its order of magnitude is much smaller than that of the surface or interfacial tensions. However in the case of adhering drops of liquids to liquids or solids (very low interfacial tensions), the stabilising effect of the line tension may become dominant.

### Experimental

The L.C studied is: 4-4' pentyl-cyanobiphenyl (5CB). Asymmetric thin films, less than several microns, are spread on the water surface. The film is studied optically using a polarizing microscope and transmitted light. Metastable holes are formed inside the film. Eventually they are stable: the equilibrium state is a monolayer coexisting with a drop. The contact angle of the drop with the monolayer is  $\alpha \simeq 10^{-3}$  rd.

### Results

The film structure depends on its thickness  $b$ . For  $0,5 \mu < b < 10 \mu$ , the following nematic structure has been observed:

1. The aspect of the defects observed in the plane of the film: "noyaux" (3), walls (4), holes, allows the determination the local average orientation of the molecular axis. This orientation is radial.

2. The film thickness is uniform.

3. At the L.C-water interface the molecular orientation is parallel to the interface.

4. The molecular orientation at the L.C-air interface is either perpendicular to the interface or parallel

respectively when  $b > b_c$  or  $b < b_c$ , where  $b_c = 2,5 \mu$  is a critical thickness.

Using 3. and 4. and allowing for the bulk elastic energy of the film (5), the difference  $\Delta\gamma = \gamma_{\parallel} - \gamma_{\perp} = 5.10^{-3}$  dyne.cm<sup>-1</sup> is deduced, where  $\gamma_{\parallel}$  and  $\gamma_{\perp}$  are the surface tensions for the respective surface polymorphic structures  $\parallel$  and  $\perp$ .

5. The study of the hole stability in the thin films leads to the value of line tension

$$\varkappa \simeq 7.10^{-6} \text{ dyne.cm}^{-1}$$

This value corresponds to the deformation elastic energy in the neighbourhood of the hole.

### Conclusion

The stability of thin films is related to the effect of film thickness on film structure which may create bulk elastic tensions inside the thin film. This structure is determined by the spatial distribution of molecular axis in the thin film.

The thin films we studied may serve as models for the lyotropic L.C stabilizing microemulsions (6). Indeed interfaces stable down to  $10^{-3}$  dyne.cm<sup>-1</sup> have been observed (7). A film polymorphism and work of internal elastic tensions may decrease the interfacial tension by  $\Delta\gamma \simeq 10^{-3}$  dyne.cm<sup>-1</sup>, favour spontaneous microemulsification and stabilisation by inhomogeneous thin films. The elastic tension in these films may stabilize them and the microemulsion.

### Summary

The structure of a liquid crystal (L.C) thin film on water has been studied optically and the molecular orientation at its interfaces has been deduced. The surface tension shift  $\Delta\gamma$  corresponding to the orientations of the molecules either normal or parallel to the free surface has been deduced. From the study of the formation and of the stability of holes in the thin film we deduce the order of magnitude of the line tension  $\varkappa$ . This tension originates in the elastic deformation of LC in the neighbourhood of the hole.

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