H1. ANISOTROPIC QUENCHED DISORDER EFFECTS ON A LIQUID CRYSTAL CONFINED INTO NANOCHANNELS

R. GUÉGAN[1], R. LEFORT[1], M. GUENDOUZ[2], I. MIREBEAU[3] AND D. MORINEAU[1]

[1] Groupe Matière Condensée et Matériaux, UMR-CNRS 6626, Université de Rennes 1, 35042 Rennes, France
[2] Laboratoire d'Optronique, FOTON, UMR-CNRS 6082, 22302 Lannion, France
[3] Laboratoire Léon Brillouin (CEA-CNRS), CEA. Saclay, 91191 Gif-sur-Yvette Cedex

Intense experimental and theoretical efforts have focused on quenched disorder effects in condensed matter as they bring about some most challenging questions of modern statistical physics. Most universal features of quenched disorder effects can be envisaged in the frame of random field theories.
From this standpoint, liquid-crystals (LC) confined in random porous materials are definitively recognized as paradigm systems, which allows one to address experimentally general questions on phase transitions, critical scaling and non-ergodicity in the presence of quenched random fields [1].
LC present many different phase transitions in bulk conditions, involving a variety of universality classes and the breaking of continuous symmetries. They offer unique opportunities to test some general theoretical predictions. The smectic transition has retained a special interest because it is predicted to be unstable towards the presence of an arbitrarily weak quenched disorder. A positionally disordered but topologically ordered "smectic Bragg glass" (SBG) is even predicted in the case of anisotropic random media [2]. However, this new thermodynamically distinct low-temperature phase remains enigmatic experimentally.
LC are elastically soft materials and may directly couple to the surface of the porous matrix, which acts as an external field. Confinement in strongly disordered porous materials can be used as an experimental way to introduce an external random field coupling to the LC order parameters. Primary studies have been carried out with random porous silica (aerogels) and aerosil LC-dispersions [1,3], which lead to an almost spatially homogeneous random pinning of the LC. In the present contribution, we prove that it is possible to introduce anisotropic random fields in one-dimensional (1D) conditions of confinement [4]. These new openings rely on the use of aligned nanochannels formed in porous silicon films (PSi) [5].
Anodization of heavily p+-doped (100) oriented silicon leads to a parallel arrangement of unconnected channels (diameter: ~30 nm, length: 30 mm) running perpendicular to the surface wafer (called columnar form of the PSi). The aspect ratio of each channel exceeds 1000:1 and induces a low dimensionality (quasi 1D) to the system (cf. Fig. 1). The preferential alignment of all the channels perpendicularly to the silicon surface prevents powder average limitations when measuring anisotropic observables of unidimensional nanoconfined systems.
Under these conditions of confinement, anisotropic quenched disorder is introduced by the highly corrugated inner surface of the 1D pores, which has been proved to be strongly irregular at the microscopic length scales i.e., ~1 nm.

Fully hydrogenated octylcyanobiphenyl (8CB) has been chosen as a reference LC. It undergoes with increasing temperature the following sequence of phases: crystal (K), Smectic A (A), Nematic (N) and isotropic (I) with the following transition temperatures: T_{KA}=294.4 K, T_{NA}=305.8 K and T_{NI}=313.5 K.

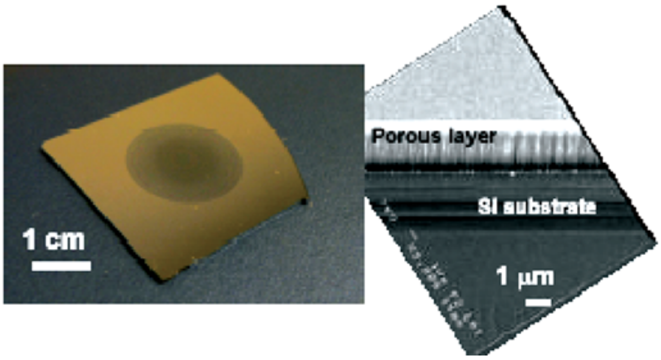

Figure 1. Top view of the porous silicon wafer (left). Side view of the porous layer by scanning electron microscopic (right)

A spontaneous alignment of the mesophases and crystalline phases has been observed in confinement. It corresponds to a preferential orientation of the nematic and smectic orderings along the pore axis, as revealed by spectroscopic ellipsometry, polarized microRaman and small angle neutron scattering (PAXY, LLB) [6]. This direct consequence of confinement has been related to the unidirectional character of the porous geometry. The nature of the surface interaction (anchoring) is not prevailing here, since changing the interaction from hydrophilic to hydrophibic by surface chemical treatment (silanization) does not affect qualitatively the overall structure and phase behaviour of 8CB in PSi [5].
A precise structural description of the confined phases requires an improved q-resolution, which can be achieved with a monochromatic cold-source double-axis neutron diffractometer (G6.1). The macroscopic parallel alignment of the porous nanochannels allows one to investigate the effects of anisotropic quenched disorder on the structure of the mesophases by selecting peculiar incidence angles so that the transfer of momentum q is practically parallel or perpendicular to the pores axis. An extreme alteration of the phase diagram of 8CB in PSi has been observed (cf. Fig. 2). Crystallization is strongly depressed on cooling and leads to two crystalline phases below 250 K, which do not correspond to any stable phase of bulk 8CB.

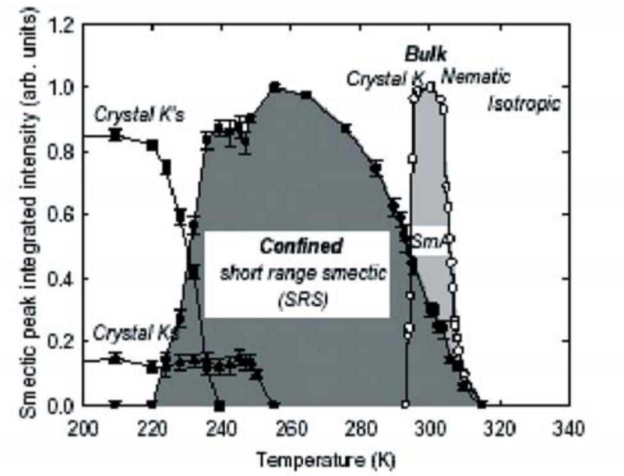

Figure 2. Phase behaviour of bulk and confined 8CB, revealed by the temperature variation of the Bragg peaks characteristic of the different phases.

More remarkable is the absence of a nematic-smectic transition, which is replaced by a reversible and gradual increase of a short-range translational order. This short range ordered smectic phase (SRS) is stable and evolves on an extremely wide temperature range down to 50 K below the bulk crystallization. Its structure factor is characterized by a single broad diffraction peak at q = 0.2Å-1, which corresponds to the location of the smectic Bragg peak in the bulk. A lineshape analysis of this peak has revealed the existence of two components, which agrees with recent random fields theoretical predictions. The first term (of Lorentzian type) dominates at high temperature and reflects the smectic thermal fluctuations also observed in the bulk. An additional term is required in the presence of quenched disorder and prevails in the SRS phase at low temperature. The fitting of the structure factor with this theoretical expression provides a smectic correlation length, which increases continuously from 3 nm at the bulk nematic-smectic transition temperature up to 12 nm at 250K (cf. Fig. 3). This variation strongly differs from what is expected for more usual nanoconfinement effects in terms of surface interaction and finite size effects.These latter effects are exemplified by the case of 8CB confined in alumina nanochannels of the same size (30 nm), which are known to present a fairly regular wall structure. In this case, the signature of a sharp transition from the nematic to the smectic phase is maintained although it is slightly rounded and depressed (about 2 K). The variation of the smectic fluctuations correlation length follows the critical behavior of the bulk, although the smectic domains are ultimately spatially limited at the transition by finite size effects. An additional independent proof of the primacy of quenched disorder effects for 8CB in PSi is the apparent linear dependence between ksi and the smectic susceptibility obtained by integration of the pseudo- Bragg peak intensity. Such a relationship, which has been predicted theoretically, points up the origin of the SRS phase. The gradual increase of short-range correlation length is resulting from the competition between the elasticity of the smectic layers and the strength of disorder introduced by the porous solid.

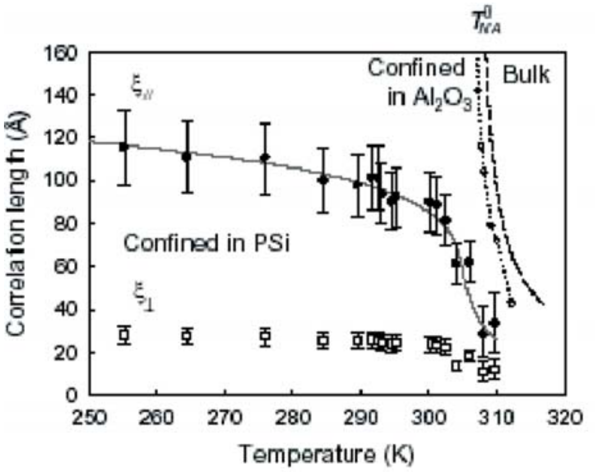

Figure 3. The temperature variation of the smectic correlation length for bulk 8CB (dashed line), for 8CB confined in porous alumina (dotted line) and for 8CB confined in porous silicon (filled circles).

The confinement of LC in PSi has opened new perspectives in the unexplored regime of anisotropic and strong quenched disorder, which may inspire future investigations. Our results already imply that much of the scenario expected for weak disorder is retained in the regime obtainable with PSi. Additional crucial aspects related to the ergodicity of the system and the occurrence of a glassy dynamics resulting from quenched disorder remain to be explored [7,8].
Financial supports from the *Centre de Compétence C.Nano Nord-Ouest, CNRS* and *Rennes Metropole* are expressly acknowledged.

[1] T. Bellini, L. Radzihovsky, J. Toner, and N. A. Clark, *Science* **294**, 1074 (2001).
[2] B. Jacobsen, K. Saunders, L. Radzihovsky, and J. Toner, *Phys. Rev. Lett.* **83**, 1363 (1999) ; L. Chen and J.Toner *Phys. Rev. Lett.* **94**, 137803 (2005).
[3] R. L. Leheny, S. Park, R. J. Birgeneau, J.-L. Gallani, C. W. Garland, and G. S. Iannacchione, *Phys. Rev.* E **67**, 011708 (2003).
[4] R. Guégan, D. Morineau, C. Loverdo, W. Béziel, and M. Guendouz, *Phys. Rev.* E **73**, 011707 (2006).
[5] R. Guégan, *PhD Thesis dissertation*, University of Rennes, France (2006).
[6] R. Lefort, D. Morineau, R. Guégan, A. Moréac, C. Ecolivet and M. Guendouz, Philos. Mag. (in press) ; cond-mat/0605112 (2006).
[7] M. Marinelli, F. Mercuri, S. Paoloni and U. Zammit, *Phys. Rev. Lett.* **95**, 237801 (2005).
[8] R. Guégan, R. Lefort, W. Béziel, D. Morineau, M. Guendouz and B. Frick, (submitted) ; cond-mat/0604353 (2006).