Orientational Quenched Disorder of a Nematic Liquid Crystal

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(Received 31 October 2009; published 4 March 2010)

By means of direct imaging, we map the surface heterogeneities of the nematic director orientation on a SiO_x anchoring layer. The spatial correlations of surface director orientations are well fitted with a compressed exponential with exponent of 1.5 and typical correlation length of few microns. To discuss these results a formal analogy is established between the equation governing the nematic surface torques and the Langevin equation. Based on this analogy we prove that the disorder is spatially correlated orientational quenched disorder. The measured correlation length is discussed in terms of substrate morphology and molecular adsorption.

DOI: 10.1103/PhysRevLett.104.097801 PACS numbers: 61.30.Hn, 61.30.Gd, 61.30.Pq

Quenched disorder refers to a disorder which is frozen; i.e., it does not change in time. In most experimental situations, this noise has a peculiar statistical signature with correlations decaying on some finite length as opposite to uncorrelated and scale invariant white noise [1]. Despite this lack of universality, correlated quenched disorder is ubiquitous in condensed matter [2–5]. In systems with orientational degrees of freedom like ferromagnets [2,6], ferroelectrics [3,7], and liquid crystals [8,9], orientational quenched disorder (OQD) profoundly affects the dynamics and the phase order of these systems. The influence of OQD on the phase order has been principally studied in liquid crystal (LC). In particular in nematic LC elastomers, OQD decreases the discontinuity of the nematic-isotropic transition [10]. Similar effects have been observed in systems with large surface/volume ratio as aerosil matrices infiltrated with LC. In these systems, OQD competes with the nematic long-range order [8,11,12] and changes the critical exponents in smectic [13]. Unfortunately a direct characterization of these surface random fields necessary for an overall understanding of the measured phenomena is still lacking.

The importance of OQD has equally been demonstrated in domain coarsening dynamics of these systems. In Ising ferromagnets, theories show that the orientational domain's growth after a magnetization reversal is affected by OQD [14]. On the experimental side, the measurement of the average magnetization and direct imaging of the spin orientation [2] confirm the central role of OQD in these dynamics. In liquid crystals, special attention has been paid to the coarsening dynamics of nematic reverse tilt domains [9] and to the defects' dynamics over alignment layers [15]. Shenoy *et al.* [9] argued that the measured dynamics should be controlled by surface heterogeneities from submicron up to optical scales in the alignment layer. More recently, Radzihovsky *et al.* [16] predicted using an *xy* model that even a weak surface disorder on the symmetry axis of the system can penetrate on macroscopic length inside the LC bulk. Despite these pioneering works, the exact role of the disorder on the dynamics of these condensed matter systems is still lacking. Obviously the necessary step to fully address this problem is the direct characterization of the disorder. In crystals, these kinds of measurements are difficult to realize due to the typical microscopic length scale of the heterogeneities [17]. In this respect, a nematic LC is the system of choice as the quenched heterogeneities scale up to easily accessible optical scales.

In this Letter the OQD is directly measured and its spatial correlation function established for the first time by direct imaging of the surface orientations of a nematic liquid crystal. A formal analogy with the Langevin equation proves unequivocally the correlated character of the measured disorder.

The experiment is done with samples consisting of a few micrometers thick (about 10 μm) nematic liquid crystal cell made by a planar anchored plate assembled with a homeotropic counterplate. The planar homogeneous anchoring is obtained by evaporating at 60° a 15 nm SiO_x layer on float glass plates [18]. To obtain an homeotropic anchoring, a solution of silane (0.1% vol/vol of 3-(trimehoxysilyl) propyldimethyloctadecyl ammonium chloride in methanol) is spin coated on glass slides and then baked for 1 h at 110 °C [19]. The cell is filled with the 4-*n*-pentyl-4'-cyanobiphenyl (5CB) nematic liquid crystal (from Synthon) in its isotropic phase. Observations are led under a transmission polarizing microscope equipped with a 1024×768 pixel^2 monochromatic 10-bit CCD camera. The overall magnification is such that a side of a camera pixel corresponds to 0.28 μm. The temperature of the cell is controlled by means of a microscope hot stage (Instec) stabilized at 0.03 °C.

Between crossed polarizers, the minimum intensity transmitted through the cell is obtained when the normal to the SiO_x evaporation plane is parallel to one polarizer. For such an orientation, the transmitted light is, however, not perfectly extinct. A weak heterogeneous intensity distribution is observed across the sample. From this intensity

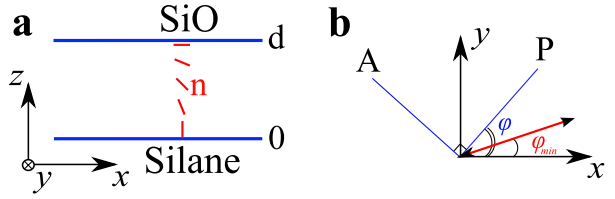

FIG. 1 (color online). Sketches (a) of the used planar or homeotropic geometry (the x axis is defined as the average easy axis on SiO_x) and (b) of the angles φ and $\varphi_{\min}$ of the polarizer and the minimum transmitted intensity with respect to the x axis.

it is possible to isolate the local director orientation on the SiO_x surface. The local easy axis of the homeotropic substrate is indeed perpendicular to the incident light beam, and the transmitted intensity through the cell is sensitive only to the director orientation on the SiO_x-treated surface [cf. Figure 1(a)]. First an average of about 100 frames taken at 1 frame per second is necessary to get rid of the temporal fluctuations coming from thermal director fluctuations in bulk and to obtain a stationary intensity map. This procedure is repeated for each angle φ in the $\pm 18°$ range between the polarizer and the x axis [Fig. 1(b)]. For each pixel corresponding to the (x, y) location, the intensity dependence on φ allows us to accurately obtain the angle $\varphi_{\min}(x, y)$ of minimum local transmitted intensity through the fit:

$$I(\varphi) = I_0 \sin^2 2(\varphi - \varphi_{\min}), \quad (1)$$

where I_0 is an intensity amplitude. The angle of minimum intensity is directly related to the surface director angle φ_s through $\varphi_s = 2\varphi_{\min}$ [20]. We thus obtain a map $\varphi_s(x, y)$ of the azimuthal orientation of the angular field of the director on the SiO_x layer.

Such a map is shown in Fig. 2 with a color representation of φ_s. This picture reveals the presence of angular domains: the blue (black) ones correspond to the highest values of φ_s, and the green (gray) ones to the lowest values. The distribution of orientations taken on 20 different samples is a normal distribution around 0° with a typical mean standard deviation $\sigma = 0.7° \pm 0.1°$ (inset of Fig. 2) comparable to the one measured on polytetrafluoroethylene substrates [21].

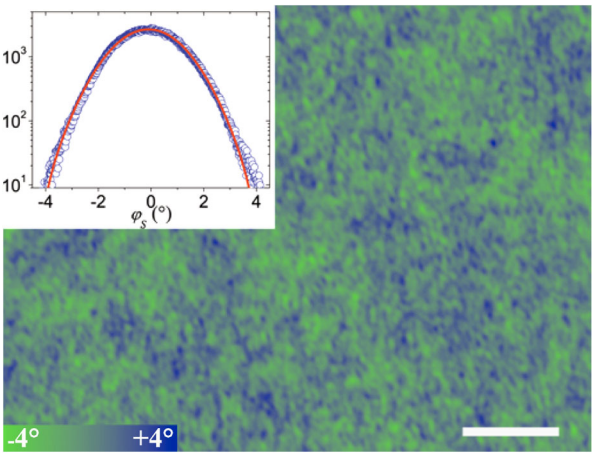

FIG. 2 (color online). Typical map of the surface director angles φ_s shown in color representation. Bar is 50 μm. Inset: Histogram of φ_s fitted with a Gaussian function.

To extract more statistical information from these angular maps, a 2D spatial autocorrelation (AC) function is computed via the inverse Fourier transform of the power spectral density (PSD). A typical PSD of director angles is represented in the inset of Fig. 3. One can notice that the PSD is isotropic, which means that the easy axis anisotropy is not reflected in the domain's morphology. The radial autocorrelation functions $C(r)$ are obtained by angular integration at fixed r of the 2D AC functions. Figure 3 shows typical ACs of two different regions of the surface. The two ACs are well superimposed in the region 0–3 μm, and differ significantly at larger spatial lags. All the measured ACs show the same behavior. In the following the focus will be made on the short (≤ 3 μm) spatial lags of the AC curves.

The ACs are not exponential but are best fitted by a compressed exponential $C(r) = \exp[-(r/a)^b]$ with correlation length a and compression exponent b. The mean values of fit parameters on more than 100 maps are $a = 3 \pm 0.5$ μm and $b = 1.5 \pm 0.1$ (the roughness exponent $b/2 = 0.75$ is in the range of values measured in other systems [1,22]). In principle, the correlations should be affected by the diffraction limited optical resolution. To test the influence of diffraction, all of the process to reconstruct the surface director mapping has been repeated on deconvoluted intensity images, with an experimentally determined point spread function. This function is measured through the optical response of small enough latex beads of 0.1 μm radius. This procedure leads to a very low correction (<1%) on the fitting parameters.

The influence of temperature on the angular domains has also been investigated. Figure 4 shows the evolution of

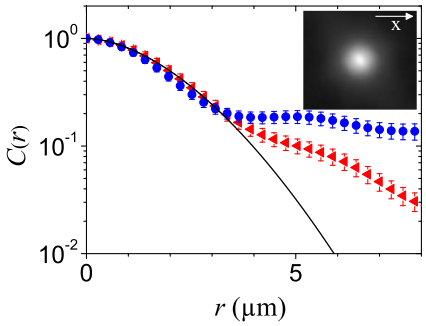

FIG. 3 (color online). Autocorrelation function $C(r)$ of two different angular maps. Also shown is the best fit (full line) with the function $C(r) = \exp[-(r/a)^b]$ of one experimental curve (red triangles), with $a = 3.27 \pm 0.06$ μm and $b = 1.54 \pm 0.03$. Inset: A 2D power spectral density of an angle's mapping.

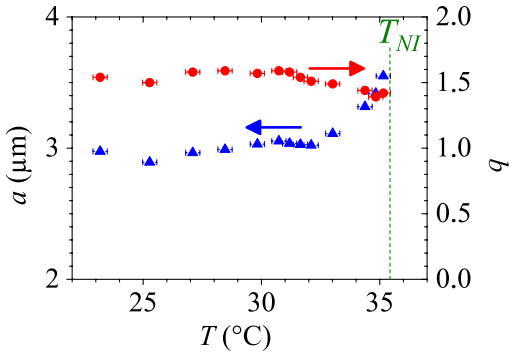

FIG. 4 (color online). Compressed exponential fit parameters versus temperature. $T_{\mathrm{NI}}(= 35.3\,^{\circ}\mathrm{C})$ is the nematic-isotropic transition temperature.

fitting parameters with temperature. The correlation length a slightly increases when approaching the clearing point T_{NI} of 5CB, while the compression exponent b remains almost constant at the value $b = 1.52 \pm 0.07$.

All these experimental facts prove the existence of a surface disorder at the 5CB/SiO_x interface. Does this disorder have the statistical signature of a correlated quenched disorder? To answer to this question let us write the director governing equations for this problem. The director is described by $\mathbf{n} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, where φ is the azimuthal angle of the director projection on the (x, y) surface plane and the x axis. θ is the zenithal angle between the director and the normal z to the surfaces. In the limit of weak azimuthal angle and in the one elastic constant approximation, the zenithal angle changes over the cell gap as $\theta(z) \approx \theta_a(z) = (\pi/2)(z/d)$. By minimizing the nematic Frank energy, one obtains for $\varphi(x, y, z)$:

$$\Delta\varphi + \frac{\pi}{d}\frac{1}{\tan\theta_a(z)}\frac{\partial\varphi}{\partial z} = 0, \tag{2}$$

with boundary condition on the planar plate under study,

$$\left.\frac{\partial\varphi}{\partial z}\right|_{z=d} + \frac{1}{L}(\varphi_s - \varphi_0) = 0. \tag{3}$$

In (3), L is the anchoring extrapolation length, and we consider weak deviations of the surface director from the easy axis ($\varphi_s \ll \varphi_0$). In the limit of uniform L, we solve (2) and (3) by using the decomposition of φ:

$$\varphi(x, y, z) = \frac{1}{2\pi}\iint f(\mathbf{q}, z)\tilde{\varphi}_s(\mathbf{q})\exp^{-i\mathbf{q}\cdot\mathbf{r}_\perp}d\mathbf{q}, \tag{4}$$

where $\mathbf{r}_\perp = (x, y)$, $\mathbf{q} = (q_x, q_y)$, $\tilde{\varphi}_s(\mathbf{q})$ is the Fourier transform of $\varphi_s(x, y)$, and $f(\mathbf{q}, z)$ gives the functional dependence of φ with respect to z. By replacing φ in (2) and by using $\partial f/\partial z|_{z=0} = 0$ (no azimuthal torque on the homeotropic plate) and $f|_{z=d} = 1$, one obtain for $f(\mathbf{q}, z)$:

$$f(\mathbf{q}, z) = \frac{\sin(\sqrt{1-\alpha^2}\frac{\pi z}{2d})}{\sin(\sqrt{1-\alpha^2}\pi/2)}\frac{1}{\sin\frac{\pi z}{2d}}, \tag{5}$$

where $\alpha = 2qd/\pi$. For $qd \gg 1$, the Fourier transform of the boundary condition (3) is written as

$$iq\tilde{\varphi}_s(q) = -\frac{1}{L}\tilde{\varphi}_s(q) + \frac{1}{L}\tilde{\varphi}_0(q), \tag{6}$$

and finally

$$\tilde{\varphi}_s(q) = \frac{\tilde{\varphi}_0(q)}{1 + iqL}. \tag{7}$$

Equation (6) is identical to a Fourier transform of a Langevin equation. The term on the left-hand side is the inertial contribution. On the right-hand side, $-\tilde{\varphi}_s(q)/L$ is a viscous term and $\tilde{\varphi}_0(q)/L$ is the *noise* term interpreted as a random force. From the solution of (6) in a mean square form [23] we can easily obtain the AC for φ_s at lag space r:

$$C(r) = 1 - \frac{\exp(-2r/L)}{L^2\sigma^2}\int_0^r\int_0^r \exp\left(\frac{r_1 + r_2}{L}\right) \times\langle\varphi_0(r_1)\varphi_0(r_2)\rangle dr_1 dr_2. \tag{8}$$

For uncorrelated Gaussian disorder, $\langle\varphi_0(r_1)\varphi_0(r_2)\rangle = \sigma^2\delta(r_1 - r_2)$, where δ represents the Dirac function and $C(r) = \exp(-\frac{2r}{L})$. In this case, the surface director orientations are expected to be correlated on a distance of the order of the anchoring extrapolation length which is the sole characteristic length of the problem ($L = 0.07$ μm at $T = 25\,^{\circ}\mathrm{C}$ for SiO_x in the same evaporation conditions [24]). Opposite to this prediction, the experimental ACs follow a compressed exponential on length scale 2 orders of magnitude larger than L. This indicates that $\langle\varphi_0(r_1)\varphi_0(r_2)\rangle \neq \delta(r_1 - r_2)$: the disorder is quenched correlated non-Gaussian with a specific length different from L but related to the liquid crystal surface [25]. In the limit $qd \gg 1$ used to deduce (6), the obtained results are independent from d.

The assumption of uniform L used to deduce (8) is justified in the limit of our experiment: typical elastic torques on the surface [left-hand side in (6)] scale as $q \approx 2\pi/a = 2$ $\mu\mathrm{m}^{-1}$ which is almost 1 order of magnitude lower than the typical anchoring torques $\propto 1/L \approx 14$ $\mu\mathrm{m}^{-1}$ [first term on the right-hand side in (6)]. An important consequence is that the surface director coincides with the easy axis and the measured noise comes essentially from the easy axis distribution. The measured increase of the correlation length with temperature is in qualitative agreement with (7) if one considers the temperature dependence of L reported in [24] and a temperature independent φ_0.

Let us now discuss the possible origins of this orientational quenched noise. We have shown that OQD is related to the statistical properties of the easy axis distribution. In general, the easy axis orientation on a solid substrate may depend on the morphology and on the physical-chemistry properties of the surface and also on the presence of oriented layers of adsorbed liquid crystal molecules. The peculiar morphology of the bare SiO_x surface has been

studied by atomic force microscopy (AFM) [26] and more recently by transmission electron microscopy [27]. The AFM images reveal the presence of surface clusters of average height of 2 nm and typical width of 50 nm. The height's correlation function is self-affine with exponent 1.5 close to the exponent of our angle autocorrelation functions. AFM measurements made on our samples show exactly the same behavior. Despite a close exponent value, to fully ascribe the measured OQD to SiO_x morphology alone one needs also to match the measured value of correlation length of 3 μm and the typical angular dispersion of 1°. To this scope, we implement an anchoring model in the vein of the Berreman one [28]. In the model the local easy axis results from a balance between a microscopic anchoring torque and an elastic torque associated with the SiO_x morphology. We assume that the anchoring torque imposes an homogeneous easy axis along x with anchoring extrapolation length L due to microscopic interactions. The elastic torque is calculated by minimizing the morphology induced distortion under the experimentally justified assumption of weak roughness. By plugging in the model the measured SiO_x morphology and known value of L, we are able to reconstruct an easy axis with the same spatial resolution as the AFM scans. We found angular distribution of surface director with typical correlation length of 0.1 μm below the optical pixel size. After convolution with the optical pixel size, we obtain a histogram width in agreement with the experimental one. Note that a subpixel correlation length could be present in our system but is filtered out in our measurements due to our spatial resolution. To summarize, the morphology alone is sufficient to explain the easy axis dispersion but fails by more than 1 order of magnitude in the prediction of spatial correlation length. Let us now discuss the effect of an adsorbed liquid crystal layer. Recent measurements on polymeric isotropic substrates made anisotropic by adsorption of an oriented molecular liquid crystal layer show the importance of surface adsorption. These orienting layers present similar OQD as the SiO_x ones, i.e., same exponent and correlation length [29]. It is tempting based on these facts to conclude on the relevance of surface absorption to explain OQD. This conclusion has to be taken with caution. The characteristic of the adsorbed layer is indeed known to strongly depend on the history of the sample and, in particular, on the fashion the first contact with the liquid crystal has been established. To elucidate this mechanism we tried different preparations of the first adsorbed layer: from the gaseous, the isotropic, and the nematic phases. All these different methods give the same OQD characteristics. These observations suggest that surface adsorption alone certainly contributes to OQD but is not sufficient to explain all our results. A possible mechanism should result from the interplay between domain coarsening dynamics and surface adsorption [30].

In summary, we have carried out a direct statistical characterization of the still unexplored orientational heterogeneities of a nematic liquid crystal on a surface. In our experimental geometry, the equation governing the surface director is formally analogous to the Langevin equation describing Brownian motion. Based on this analogy, the spatial correlation functions of the surface director angle support unequivocally the presence of a correlated orientational quenched disorder. In our opinion, this direct characterization of surface heterogeneities in LC is the necessary first step toward the overall understanding of the peculiar dynamics in the general class of OQD systems in condensed matter.

We thank M. Ciccotti and M. George for the AFM measurements.

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