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Dynamics of Liquid Crystalline Domains in Magnetic Field

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We study microscopic single domains nucleating and growing within the coexistence region of the Isotropic (I) and Nematic (N) phases of a low molecular weight liquid crystal in magnetic field. After rapidly switching on the magnetic field we measure the time needed to align the nuclei of sufficiently large size along the field. We find that this time decreases with the square of the magnetic field. When the field is removed the orientation relaxation time of an aligned domain is observed to be longer. The growth rate of nematic domains at constant temperature is found to follow the predicted power law and to increase with magnetic field.

Keywords: alignment; dynamics; liquid crystals; magnetic field; phase transition

1. INTRODUCTION

The study of the properties of liquid crystals (LCs) has fascinated scientists since the early sixties [1] and has lead to new theories and new applications, making that liquid crystals have entered the daily life. Recently we have found that polymer liquid crystals can be aligned in a magnetic field, but only when the temperature is swept through the Isotropic-Nematic phase transition at fixed field, while no alignment effect is observed at fixed temperature upon sweeping the field [2]. Clearly the dynamical behaviour in a magnetic field around the phase transition is responsible for this observation; thus we study this region in more detail, using a low molecular weight LC as a model system. This phase transition region has attracted

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great attention both from the theoretical and the experimental point of view [3–7].

We define the I-N transition temperature T_{IN} as the temperature in the middle of the coexistence region, in which nematic nuclei are formed and rapidly grow in size and number, surrounded by an isotropic background, until they coalesce into the fully developed nematic phase [8,9]. We measure with polarized microscopy the behaviour of the nematic domains in the coexistence region, both at constant magnetic field to study the growth rate as well as in transient magnetic fields to monitor the dynamical magnetic alignment. Each nematic cluster consists of about thousands of correlated LC molecules with a uniaxial orientation. The majority of the clusters exhibit a preferential orientation of the internal molecules, which allows the definition of an order parameter as $S(\alpha) = < \frac{3\cos^2\alpha - 1}{2} >$, where α is the angle between the symmetry axis of the molecule and the domain director. The domain director defines the orientation of the domain as a whole and is, in the absence of an external field, randomly oriented. The size of the observed domains varies between 10 and 50 μm, which is sufficiently large to neglect the role of the molecules in the outmost layer of the domain that are in direct contact with the molecules in the Isotropic phase. The surface elasticity plays therefore no role, which is consistent with the fact that no shape variation of the clusters occurs during the alignment. We show that each nematic domain orients with its director parallel to the field direction via a rotation of the domain as a whole, with a time τ_{al} that depends on the field strength. Smaller domains need a higher field to align than bigger ones. Upon switching off the field the domains gradually relax to a random orientation due to thermal fluctuations in a time τ_{dis} that is much longer than τ_{al}. The relaxation time increases with increasing domain dimensions.

The growth of a domain at fixed temperature can be characterized by a time constant that follows a power law, with an exponent of about 0.5 at zero field, but which increases with field and is equal to 1.0 in 2 T.

2. EXPERIMENTAL DETAILS

A LC in a cuvette is mounted in a thermal oven placed in an electromagnet (max field 2 T). The oven allows forced and regulated heating and cooling, giving high temperature stability ($\Delta T \sim 0.005^{\circ}C$) and a rapid rate of change (2K/min) for small quenches (0.1–0.3 K). The sample is sandwiched between two crossed polarizers and is illuminated with a He-Ne laser (543.5 nm). A 10x magnification microscope

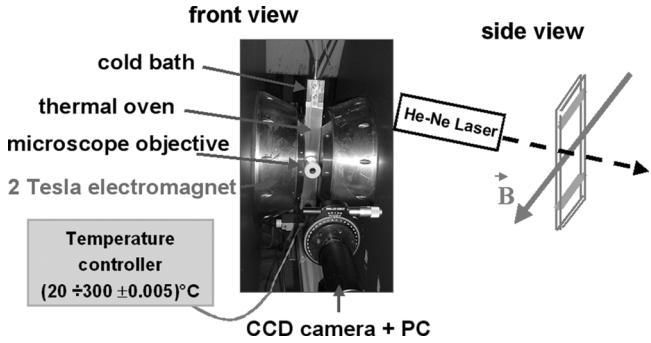


FIGURE 1 Experimental set-up to acquire images of birefringent nematic domains in magnetic field. The cross polarizers are oriented at 45 degrees with respect to the field direction, which is horizontal in the plane of the field of view.

objective is used to focus the transmitted light through the sample on a video rate CCD camera. A picture of the set-up is shown in Figure 1. The two polarizers at 90 degrees ensure that only light traversing birefringent regions of the sample is transmitted and detected, allowing the measurement of the local degree of alignment of individual nematic domains. By positioning the polarizers at 45 degrees with respect to the field direction fully aligned domains appear as the brightest, having their director parallel to the field direction. The pure liquid crystal material, the mixture MLC6610 from *Merck*, is filled in the isotropic phase by capillarity in a glass cell of thickness $\sim 500\,\mu m$; this relatively large thickness is chosen to reduce surface anchoring effects, while the use of a mixture is preferred in order to observe a sufficient broad coexistence region. With this experimental configuration we can acquire images and movies with a micrometer resolution, which we process quantitatively for each pixel in each frame. By such an analysis the light intensity is directly related to the orientation of a birefringent domain with respect to the polarizers.

3. THEORETICAL BACKGROUND

Liquid crystalline domains containing N correlated molecules exhibit an anisotropic diamagnetic susceptibility $N\Delta\chi$, where $\Delta\chi$ is the difference in magnetic susceptibility of a single molecule along directions parallel and perpendicular to the molecular axis [14]. When a magnetic field is applied, this anisotropy implies that the total magnetic energy of a domain depends on its orientation with respect to the field,

leading to an orientational force. Taking into account the randomizing effect of thermal fluctuations we write the orientation distribution function of a domain with $\Delta\chi > 0$ in magnetic field:

$$f(\alpha) = \exp\left(-\frac{N|\Delta\chi|B^2}{N_A\mu_0}\frac{1}{kT}\cos^2(\alpha)\right) \quad (1)$$

The degree of order of a domain is given by $\int_{domain} f(\alpha)\left(\frac{3\cos^2\alpha-1}{2}\right)d\alpha$. Order will therefore be induced if the magnetic energy is larger than the thermal energy, i.e.

$$N\frac{\Delta\chi B^2\cos^2(\alpha)}{\mu_0} \geq kT. \quad (2)$$

The typical domain size for which this condition is fulfilled is of the order of a micrometer in a few Tesla.

4. RESULTS AND DISCUSSION

Upon slowly cooling (0.05 K/min) from the isotropic phase, the system enters in the metastable [1] coexistence region, where nematic domains nucleate and coexist with the isotropic phase. For MLC6610 the coexistence region is $\sim$4°C broad, around $T_{I\text{-}N} = 99.65$°C. It is possible to stabilize nematic nuclei of 10 to 50 μm radius for several minutes, by keeping T constant. Under these conditions, when the magnetic field is switched on quasi instantaneously to a certain value (between 0.1 and 2 Tesla), we observe the rotation of the domain director towards the direction of the applied field.

Figure 2 shows typical snapshots of nematic domains in applied fields of 0.1 T (a) and 0.2 T (b). In these pictures the magnetic field is directed (see arrow). Aligned domains can be recognized as bright spheres with diffraction rings and two small diffraction spots left and right of the domain. At 0.2 T all domains are aligned along the field (Fig. 2b), whereas at lower field only the larger domains are aligned (see Fig. 2a, where the smaller domains indicated by the arrows are not yet fully aligned. Clearly larger domains align already at lower magnetic field. We concentrate in the following on domains that are isolated from each other and initially oriented in the viewing plane, but with their director approximately perpendicular to the magnetic field. In Figure 3a we show the change of orientation for individual domains as a function of time, for different magnetic fields. The angle of orientation θ, as defined in the inset of Figure 3a, is calculated from its proportionality with the intensity of transmitted light. All curves in Figure 3a show some initial 'waiting time', after which

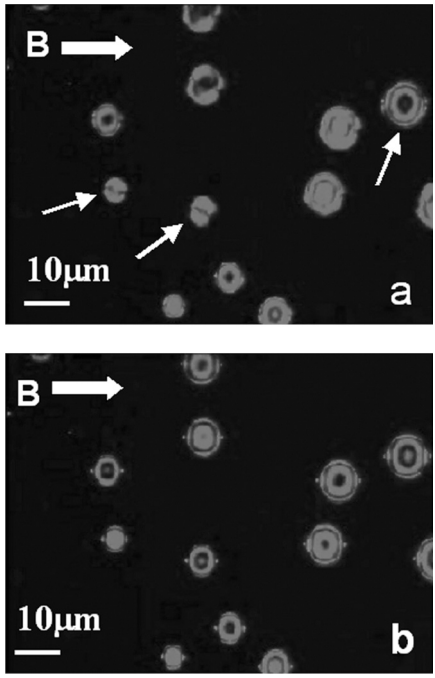


FIGURE 2 Nematic domains in a magnetic field of 0.1 T (a) and 0.2 T (b). The field is oriented horizontally.

the domains start rotating. This can be explained by considering that domains with an initial orientation at an angle almost perpendicular to the field direction can either rotate left of right. Since for small deviations from 90° the gain in energy is very small, the domain may fluctuate around its initial orientation for a while, until it moves sufficiently away from this unstable equilibrium. At this point a domain orients towards the field direction. To be more quantitative we write the equation of motion for magnetic orientation, which is the balance of the magnetic torque and the hydrodynamic torque. Assuming perfectly spherical domains we have [13]:

$$Q\frac{d\theta}{dt} = -\frac{1}{2}V\Delta\chi\mu_0 B^2\sin(2\theta) \tag{3}$$

where $V = 4\pi L^3/3$ is the domain volume, Q is the friction and θ is the angle between the domain director and the field direction. The final equation is size independence since both driving and friction torque are proportional to the volume of the domain. The solution of the

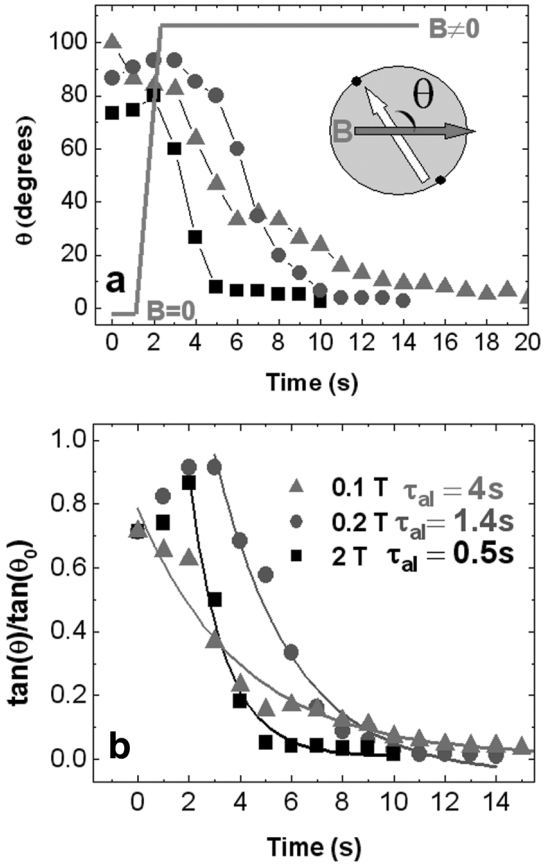


FIGURE 3 Orientation of nematic domains to the field direction ($\theta = 0$). (a) θ versus time. θ is the angle between the orientation of the domain director and the field direction, as sketched. The solid line corresponds to the field transient. (b) From the exponential fit (solid line) of $\tan(\theta)/\tan(\theta_0)$ we extract τ_{al} for each field strenght.

equation of motion is:

$$\tan(\theta) = \tan(\theta_0)\exp\left(\frac{-t}{\tau_{al}}\right), \text{ with } \tau_{al} = \frac{6\eta}{\mu_0 \Delta\chi B^2} \tag{4}$$

where η is the rotational viscosity of the material and θ_0 the orientation of the domain at the time t = 0.

In Figure 3b we plot $\tan(\theta)/\tan(\theta_0)$ for three different domains, and fit the data with an exponential function to determine τ_{al} (solid line).

τ_{al} is of the order of 4 seconds for 0.1 T and rapidly decreases by increasing the magnetic field, as expected from Eq. (4).

Switching off the magnetic field instantaneously after the domains have been aligned, we study the relaxation of the domain as a function of time. We measure a disorientation time of $\sim$3 minutes for domains of 13 μm (Fig. 4a and 4b), 7 minutes for domains of $\sim$25 mm size while domains of size $\sim$50 μm remain aligned up to 15 minutes. Clearly $\tau_{dis} >> \tau_{al}$ because in this case there is no driving force other than thermal fluctuations, which tend to randomize the orientation of the domain. Furthermore, this statistical process is found to be faster for small domains than for big domains, and roughly τ_{dis} is found to be proportional to L. This proportionality is reasonable since, with increasing domain size, the thermal disorienting force on the molecules at the interface becomes smaller compared to the number of oriented molecules inside the cluster.

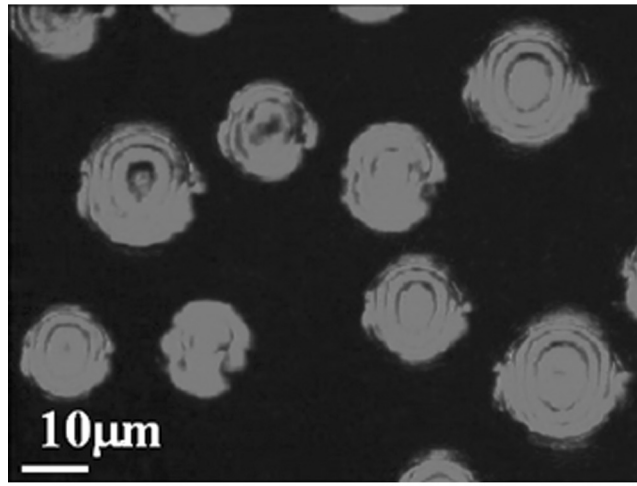
We also studied the growth rate of domains by under-cooling rapidly from the isotropic phase (0.1 K/min) to a temperature slightly below $T_{I\text{-}N}$, and then stabilize the temperature. We observe that under these conditions the probability of nucleation is rather low and only after some minutes the formation and growth of clusters of nematic clusters occurs. Consequently we can investigate the growth dynamics at constant temperature as function of field, of which typical results are shown in Figures 5 and 6. We have fitted the growth phase with a power law:

$$L(t) \sim (t - t_0)^{\beta} \tag{5}$$

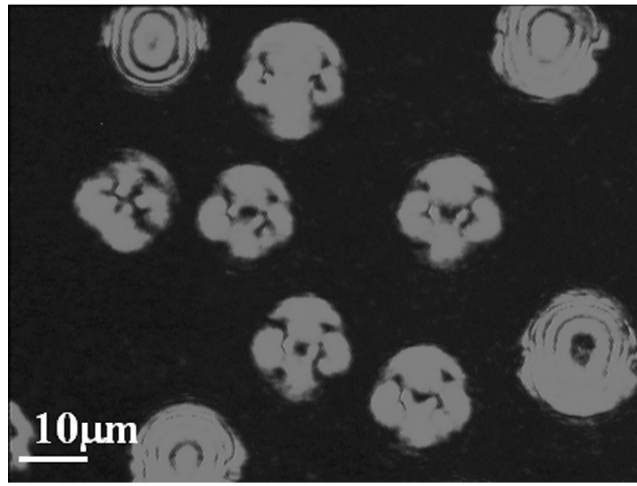
where t is time, t_0 is the time at which the domain nucleates and β is a fitting parameter. In zero field we find β to be 0.5 ± 0.2, as theoretically predicted [10,11]. In magnetic field β tends to increase from 0.5 to 1 between 0.1 Tesla to 2 Tesla (Fig. 6). Although there is a large error on the fitted exponent, mainly caused by the uncertainty in t_0, the trend of increasing growth rate in magnetic field is clear. This is an unexpected result, for which at present we have no satisfactory explanation. Since the magnetic energies are very small, we expect this faster growth to be caused by kinematical effects, rather than by a change in thermodynamic equilibrium.

5. SUMMARY

We have studied for the first time the dynamics of single nematic domains in magnetic field, near the Isotropic-Nematic phase transition. We are able to monitor the growth since its early stage and we observe



(a)



(b)

FIGURE 4 Orientation relaxation of magnetically aligned nematic. (a) domains after 180 seconds: small domains ($\sim$10 μm) have already disordered: they show irregular diffraction. (b) after 420 seconds only domains of size $\sim$50 μm are still aligned, showing diffraction rings.

at zero field a $t^{1/2}$ growth law, as theoretically predicted. In magnetic field a faster growth described by a higher exponent is observed, which is not yet theoretically understood.

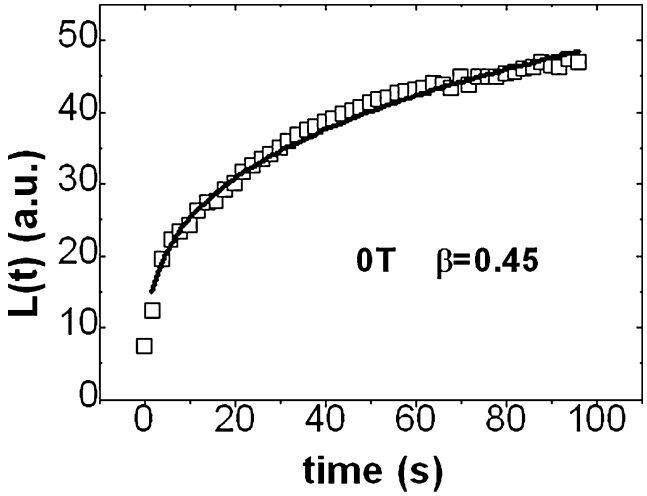


FIGURE 5 Size (radius) L of a growing domain vs time (s) without magnetic field. The size is expressed in number of pixels on the CCD camera. The line is the fit with the power law: $L(t) \sim (t - t_0)^{\beta}$.

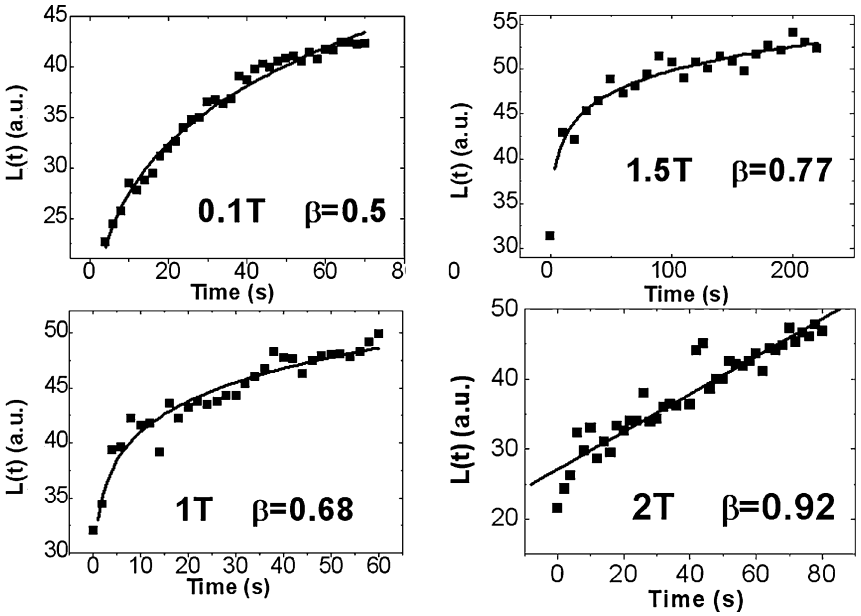


FIGURE 6 Size of a growing domain with time in different magnetic fields. The growth is fitted by a power law $L(t) \sim (t - t_0)^{\beta}$ with β increasing with field.

We have measured the time of alignment in magnetic field at constant temperature for domains of different size, verifying the predicted behaviour: $\tau_{al} \propto 1/B^2$.

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