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Magnetic Damping of Orientational Fluctuations in Nematics with Negative Diamagnetic Anisotropy

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We have studied the damping of orientational fluctuations in a magnetic field in a particular thermotropic nematic liquid crystal consisting of molecules orienting perpendicular to the applied field $\underline{H}$ ($\delta X < 0$). By aligning the average molecular axis (director $\underline{n}$) perpendicular to $\underline{H}$ and measuring the birefringence with light propagating along $\underline{n}$, we observed for the first time a single domain biaxial thermotropic nematic. The birefringence, as appearing in a magnetic field, agrees with fluctuation theory, its temperature dependence being accounted for by the temperature behaviour of the effective elastic constant K and the order parameter S.

Introductional Theoretical Approach

In nematic liquid crystals [1] the elongated molecules tend to align parallel to each other, with a common axis labeled by the director $\underline{n}$. The states $\underline{n}$ and $-\underline{n}$ are indistinguishable. Nematic liquid crystals are fluid, i.e. positional correlations between molecules are very short range like in simple liquids. In nematics it is possible to generate three different distortions : splay, twist and bend [1]. The corresponding elastic constants are K_1 for splay, K_2 for twist and K_3 for bend. As in a spring system the energy related to these distortions is given by

$$F_{el} = 1/2 \int d^3r \; [\; K_1(\mathrm{div}\;\underline{n})^2 + K_2(\underline{n}\;\mathrm{curl}\;\underline{n})^2 + K_3(\underline{n} \times \mathrm{curl}\;\underline{n})^2 \;] \qquad (1)$$

where the integral is over the volume of the sample. Such deformations may be induced by a mechanical torque and/or by the torque on diamagnetically anisotropic molecules by external applied magnetic fields. The magnetic susceptibility anisotropy δX is defined as

$$\delta X = X_{\parallel} - X_{\perp} \quad , \qquad (2)$$

where $_{\parallel}$ and $_{\perp}$ refer to respectively parallel and perpendicular to $\underline{n}$. The nematic orientational order parameter S can be related to the magnetic susceptibility anisotropy by

$$S = \delta X/\delta X_o \quad , \qquad (3)$$

where δX_o is the magnetic susceptibility anisotropy of a perfectly aligned sample. The magnetic energy related to orientation is

$$F_M = -\,1/2 \int d^3r \;\delta X\; (\underline{n}\underline{H})^2 \quad . \qquad (4)$$

For nematics with positive or negative δX the free energy will be minimized by $\underline{n} \parallel \underline{H}$, $\underline{n} \perp \underline{H}$ respectively. In the case of a competition between wall-alignment and magnetic field alignment there will be a transition layer of a certain thickness, called the magnetic coherence length f. f is given by balancing elastic energy and magnetic energy [1], resulting in

$$f(H) = (K_i/|\delta X|)^{1/2} H^{-1} \tag{5}$$

where i indicates the involved distortion and $H = |H|$. The magnetic field for which f is equal to the thickness d of the nematic slab is called the Fredericksz field H_c. A typical value for H_c is 1 T for d = 10 μm, $\delta X \approx 10^{-7}$cgs and $K_i \approx 10^{-6}$cgs. Because of the finite temperature, the orientation of the molecules will fluctuate arbitrarily around the average direction. To express these fluctuations we take the average direction along y and assume small fluctuation amplitudes

$$n = (n_x, n_y, n_z) \quad , \tag{6}$$

where $|n_x|$, $|n_z| \ll 1$, $|n_y| \approx 1$. Because of these orientation fluctuations there is a deviation from perfect alignment, which corresponds to an increase of the free energy :

$$\delta F = \delta F_{el} + \delta F_M \quad . \tag{7}$$

De Gennes [2] has given a theoretical approach to the effect of a magnetic field applied parallel to the optical axis ($\parallel \underline{n}$) of an aligned nematicum with $\delta X>0$ using the one-(elastic)-constant approximation. Malraison et al. [3] generalized this theory to three different elastic constants. In our case ($\delta X<0$) and for a magnetic field applied perpendicular to the optical axis, we have

$$\delta F = 1/2 \int d^3r \; [K_1(\delta n_x/\delta x+\delta n_z/\delta z)^2+K_2(\delta n_x/\delta z-\delta n_z/\delta x)^2 + K_3\{(\delta n_x/\delta y)^2+(\delta n_z/\delta y)^2\}+\delta X(n_z H)^2] \tag{8}$$

with $\underline{H} \parallel z$. Using Fourier components of $\underline{n}$ and the one-(elastic)-con stant approximation

$$K_1 = K_2 = K_3 = K \tag{9}$$

we find

$$\delta F = 1/2V \int_q [(Kq^2)n_x^{\,2} + (Kq^2 + \delta XH^2)n_z^{\,2}] \quad , \tag{10}$$

where $q^2=q_x^{\,2}+q_y^{\,2}+q_z^{\,2}$ stands for the wavevector q. Applying the equipartition theorem and assuming the nematicum to be a continuum, with a low frequency cut-off q_{min} given by the thickness d of the nematic slab and a high frequency cut-off q_{max} given by the distance a between two neighbouring molecules we finally obtain [4]

$$\langle |n_x(r)|^2\rangle - \langle|n_z(r)|^2\rangle \approx (1/4\pi)\, k_B T(1/Kf) \tag{11}$$

The magnetic field induced optical birefringence (Fig.1) is given by

$$\delta N = N_x - N_z \quad , \tag{12}$$

N_x, N_z being the refractive index for light polarized in x, z respectively. This leads to

$$\delta N \approx (1/8\pi)\; \delta\epsilon/\surd\epsilon_{\perp 0}\; k_B T\; (1/Kf) \tag{13}$$

where $\epsilon_{\perp 0}$ is the dielectric constant perpendicular to $\underline{n}$ and $\delta\epsilon_o$ is the dielectric constant anisotropy, both in a perfectly aligned sample.

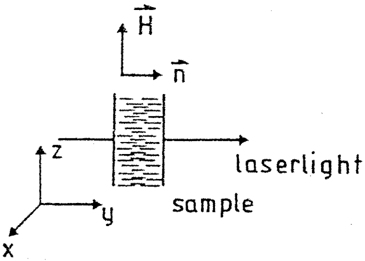


Figure 1. The geometry of our experiment. Birefringence is induced by the magnetic field in the isotropic x-z plane of the nematic.

With [5] we can estimate

$$\delta N \approx 3 \times 10^{-5} \quad \text{for } H = 10 \text{ T} \tag{14}$$

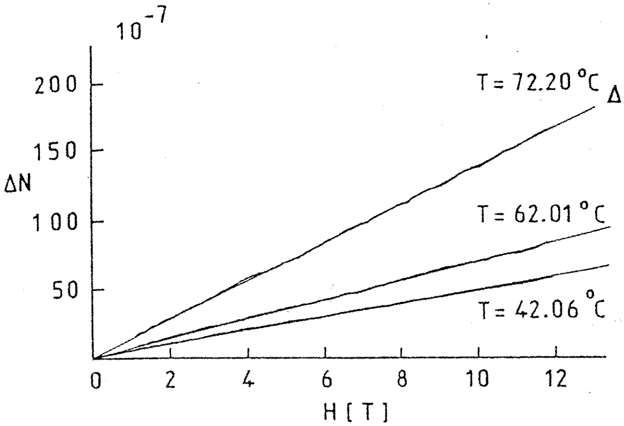
Therefore, in the experiment, both high magnetic fields and a system which can measure birefringence very accurately are necessary.

Experiments and results

Experiments on the reduction of orientation fluctuations in nematics with $\delta X>0$ have been performed before by Poggi and Filippini [6] and by Malraison et al. [3] on samples with $\underline{n}$ aligned parallel to the applied magnetic field and light propagation normal to $\underline{H}$. Magnetic quenching of director fluctuations occurs perpendicular to the field and so the magnetic field has effect in two dimensions. This geometry bears the experimental disadvantage that a small increase δN has to be measured on a large birefringence background [$\delta n(H=0) \approx 0.2$]. In our experimental geometry with nematics with $\delta X < 0$ (Fig.1), however, there is no zero field birefringence background in case of well-aligned samples, $\delta n(H=0)=0$. The molecules align in a plane perpendicular to the magnetic field and there is a reduction of the orientation fluctuations parallel to the field meaning that the influence of the field is one-dimensional. We introduce an extra third (independent) axis.

The nematic liquid crystal used (reference number ZLI 1695, Merck) is an eutecticum of several p-cyano-p'-alkylcyclohexyl-cyclohexanes (CCH) with different lengths. The absolute value of the diamagnetic susceptibility along the long axis of the molecules is larger than its perpendicular value, so $\delta X<0$. The nematic region is situated between 13°C and 72°C. A homeotropic alignment was obtained by surface treatment of glassplates, with the long-chain alcohol hexadecanol-1 . The sample thickness was 180 μm. The magnetic bi-refringence experiment [7] consists in an automatic compensation of the birefringence of the sample by the birefringence of a Pockels cell. Higher accuracy ($\delta N \approx 10^{-7}$ for our measurements) was achieved by using a photoelastic modulation technique.

The birefringence, caused by the magnetic damping of orienta-tional fluctuations, is given in Fig. 2 as a function of magnetic field for different temperatures. For all measured temperatures this birefringence was found to be proportional to the magnetic field, as expected from equation (13). The absolute value of δN is of the same order of magnitude as theoretically estimated in (14).The slope of δN turns out to be temperature dependent. Fig. 3 shows the temperature dependence of the magnetic field induced birefringence in more detail. For clearness the parameter $\delta N\, T_c/T$ at $H = 10$ T has been



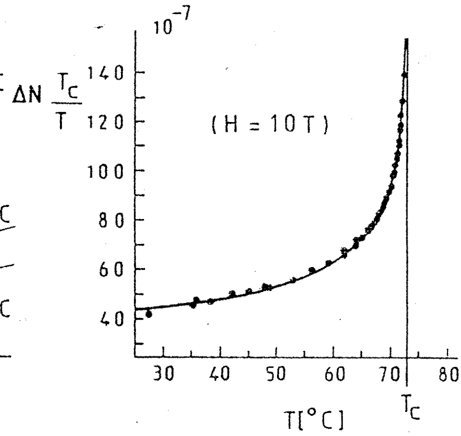


Figure 2. The birefringence, caused by magnetic damping of orientational fluctuations as a function of magnetic field, optical wavelength = 632.8 nm.

Figure 3. The normalized birefringence, caused by magnetic damping of orientation fluctuations as a function of temperature. The full curve is the fit $a_1[(T_c-T)/T_0]^{a_2}$ with $a_1=1.26\ 10^{-5}$, $T_0=1K$, $T_c=72.9°C$ and $a_2 = 0.27$.

plotted. The curve clearly deviates from a straight line parallel to the temperature axis which was expected from (13) for a temperature independent Kf value. This temperature dependence may be ascribed to the fact that nematics will become weaker upon raising the temperature, in particular when approaching the nematic isotropic transition temperature T_{NI}, i.e. the elastic constants decrease towards T_{NI}. Therefore, the order parameter S itself is temperature dependent, typically decreasing from S=0.7 at temperatures well below T_{NI} to S=0.35 near T_{NI}, hence lowering δX. The full curve in Fig.3 is a fit based on the one- (elastic) - constant approximation. It seems to describe the results rather well. Work is in progress to compare these results with independent measurements of $\delta X(T)$ and $K(T)$.

Conclusion

By means of high magnetic fields, director fluctuations can be quenched. Using molecules with negative diamagnetic anisotropy we have observed in thermotropic nematic liquid crystals biaxiality for the first time. The magnetic field induced birefringence turns out to be proportional to the applied field. Its strong non-linear temperature dependence may be ascribed to the combined temperature dependence of the elastic constants and the order parameter. The one-(elastic)-constant approximation seems to be applicable.

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