Nematic liquid crystals in high magnetic field: Quenching of the transverse fluctuations

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The partial quenching of the fluctuations of orientation of nematic layers by very large magnetic fields predicted by de Gennes and leading to increased birefringence has received a first experimental verification by Poggi and Filippini. In this paper a detailed account of this effect is given: the progressive disappearance of the induced-excess-birefringence (IEB) effect near a second-order smectic transition is connected quantitatively with the divergence of the bend elastic constant. As the isotropic phase is approached from below, the increase of IEB is connected with the decrease of the elastic constants. The IEB varies with field as $|H|^u$ with $u = 1 \pm 0.02$ over the whole nematic range. This critical-exponent determination is closely connected with the problem of the divergence of the longitudinal susceptibility in magnetic systems where both "semiclassical" and renormalization-group approaches predict a divergence in $H^{-1/2}$ in three dimensions. As no data seem to be available for the magnetic problem, the linear form obtained here provides a first experimental test of the validity of both approaches based on the quenching of transverse magnetization fluctuations by a field. Departures from the de Gennes model observed near T_{NI}, as well as deviations of the induced birefringence, observed in the same experiments, from the mean-field behavior in the isotropic phase above the nematic transition, emphasize the need for new theoretical description of this weakly first-order phase transition.

I. INTRODUCTION

In the nematic liquid-crystal phase elongated (cigarlike) molecules are aligned along an average molecular direction, characterized by the director field $\vec{n}(\vec{r})[|\vec{n}(\vec{r})|=1]$. The optical axis of the positive uniaxial phase is parallel to $\vec{n}(\vec{r})$ at each point. An instantaneous picture at the molecular level should look like the picture in Fig. 1: Figure 1(a) refers to a temperature close to the first-order transition to the isotropic phase at a temperature T_{NI}; Figure 1(b) is obtained at a lower temperature. The effect of the fluctuations of orientation is particularly large at high temperatures. It can be expressed by the scalar order parameter

$$S(\vec{r}) = \tfrac{1}{2}\langle 3\cos^2\theta(\vec{r}) - 1\rangle , \tag{1}$$

θ being the angle between the direction of any given molecules and $\vec{n}$.

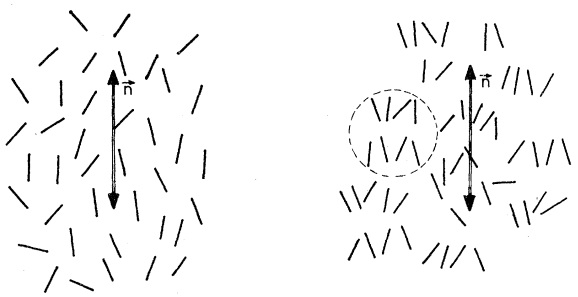

FIG. 1. Schematic representation of an instantaneous distribution of molecules in the nematic plane near T_{NI} ($S=0.35$) and T_{AN} ($S=0.75$). (The subscript indices NI and AN stand for nematic isotropic and smectic A nematic, respectively.) In the latter case we have represented a fluctuating cybotactic group whose growth explains the freezing of the transverse orientation modes in 8CB.

Figures 1(a) and 1(b) correspond to values of the order parameter $S(\vec{r})=0.35$ and 0.7, respectively. The temperature variation of $S(\vec{r})$ could be deduced from that of the magnetic-susceptibility tensor χ which is the correct form of the nematic order parameter

$$S(\vec{r}) = \chi_a/\chi_{a0} , \tag{2}$$

where $\chi_a = \chi_{\parallel} - \chi_{\perp}$; $\parallel$ and $\perp$ refer to directions respectively parallel and perpendicular to $\vec{n}(\vec{r})$; χ_{a0} would be the value of the susceptibility of a perfectly aligned sample. Figure 2 gives the temperature variations of χ_a for the two compounds used in the present experimental study.

The value $\chi_{a0} = 1.47 \times 10^{-7}$ cgs has been determined from the measurements on an oriented glass phase.[1] The positive value of the anisotropic susceptibility χ_a is due to the existence of the central aromatic rings of the molecule (expanded formulas are given in the inset of Fig. 2) which tend to favor the alignment of the molecules along the magnetic field H.

Figure 1(b) corresponds to a temperature slight-

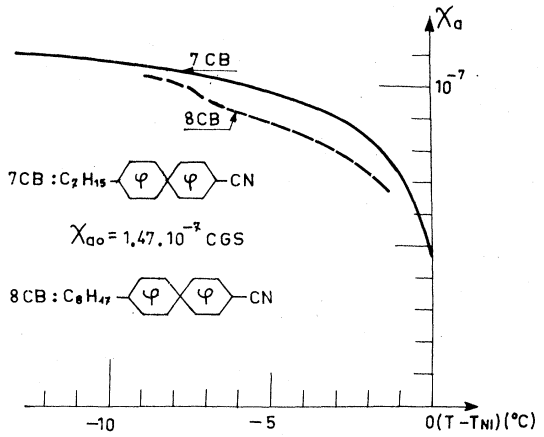

FIG. 2. Temperature variation of the anisotropic part of the susceptibility for the two compounds (Ref. 33). The value χ_{a0} has been measured in a perfectly aligned glassy sample of 7CB. We assume that the same value applies to 8CB as the anisotropy results from the central part of the molecule which is identical for both materials.

ly above the second-order phase transition, a smectic-A phase at a temperature T_{AN}. It shows the development of fluctuating smecticlike regions, the cybotactic groups, whose existence has been proved from x-ray measurements.[2] The progressive development of the smectic order rigidifies the structure of the nematic phase and limits the fluctuations of orientation. Note that there are two contributions to the fluctuations, a macroscopic or collective one related to the elasticity and a microscopic or local one. Approaching the smectic-A phase, only the former is reduced. In particular, there seems to be no discontinuity at the transition of the order parameter $S(\vec{r}) = \chi_a/\chi_{a0}$ which remains smaller than unity in the smectic phase.

It is the purpose of the present article to study these fluctuations of orientation from the response of the material to large fields. A magnetic field, applied parallel to $\vec{n}$, reduces the fluctuations of orientation and consequently causes an increase of the order parameter $S(\vec{r})$. Such an effect was predicted by de Gennes[3] and subsequently studied experimentally by Poggi and Filippini.[4] The preliminary experiments indicated a linear increase of $S(\vec{r})$ with H measured from that of the optical birefringence, $\Delta n = n_{\parallel} - n_{\perp} \sim 0.2$. This is a rather small effect $[\Delta n(H = 10^5\ \text{Oe}) - \Delta n(H = 0) \sim 10^{-4}]$ and was studied using the facilities of the Service National des Champs Intenses and of the Max Plank Institüt für Festkörperforschung in Grenoble.

The present work gives a detailed account of the experiment, including a first study of the temperature variation of the effect: When the smectic phase is approached, the freezing of the elastic fluctuation modes is found to cause a progressive decrease of the induced excess birefringence (IEB) to zero. In the high-temperature limit the IEB increases sharply as the elastic constants decrease near the isotropic phase.

The plan of the article is as follows. In Sec. II we extend the original de Gennes model[3] to include the effect of anisotropic elasticity. This extension is needed in order to describe the behavior near T_{AN}. The hypotheses embedded in this "semiclassical" approach are compared with the problem of the longitudinal magnetic susceptibility, which has received a considerable theoretical interest over the last 20 years. In Sec. III we discuss the experimental techniques used. Section IV contains a description and discussion of the experimental results which agree quantitatively with the approach of Sec. II over most of the nematic range. Emphasis is put on deviations observed near the nematic-isotropic transition. Some analogies are established with the magnetic case but no detailed description of the approach of the phase is available beyond the mean-field treatment whose deficiencies are mentioned. Finally, in the Appendix we discuss the effect of an alignment of a nematic sample in a magnetic field not parallel to $\vec{n}$. The aim of this final discussion is threefold: (i) the Freedericksz transition measurements lead to a determination of the elastic constants used in the present work, (ii) the effect of an accidental misalignment in the nematic phase must be subtracted from the IEB one; (iii) the Appendix stresses the deep fundamental unity between the static reorienting "field effect" and the dynamic effect of the reduction of fluctuations, both of which can be understood using the concept of a magnetic-correlation length varying as H^{-1} in the field.

II. THEORETICAL APPROACH

A. Nematic problem

The fluctuations of orientation of a nematic can be probed directly by light-scattering techniques. The experiments of Chatelain[5] have given a direct probe of the spontaneous fluctuations. Later the Orsay Liquid Crystals Group[6] study of the light diffused by the fluctuations was used for a quantitative study of the viscoelasticity of the nematic phase.

De Gennes[3] has considered the effect of a magnetic field parallel to the optical axis of a uniformly aligned nematic film. We generalize the calculation, which was performed with only one elastic constant K, to include Frank's three elastic constants K_1, K_2, and K_3 (see Fig. 3; the definitions of the constants are given in the Appendix).

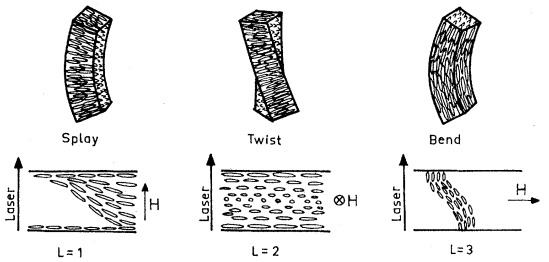

FIG. 3. The three elastic mode distortions. They can be simply visualized from the distortion pattern obtained just above the critical field H_{ci} or from a plot similar to Fig. 4.

In the presence of small fluctuations of components n_x and n_y of the director $\vec{n}$ initially aligned along the direction of $\vec{H}$ parallel to the z axis ($|n_x|, |n_y| \ll 1$), the increase of the free energy from the undistorted state ($|n_x| = |n_y| = 0$) can be calculated from formulas (A2) and (A3) as

$$2\Delta F = \int_V \left[K_1 \left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y} \right)^2 + K_2 \left(\frac{\partial n_y}{\partial x} - \frac{\partial n_x}{\partial y} \right)^2 + K_3 \left(\frac{\partial n_x}{\partial z} + \frac{\partial n_y}{\partial z} \right)^2 + \chi_a H^2 (n_x^2 + n_y^2) \right] d^3r , \tag{3}$$

where V is the volume of the sample. The first three terms represent the splay, twist, and bend elastic-energy contributions which oppose the fluctuations; the last term is the aligning magnetic-field effect.

It is convenient to Fourier analyze $n_x(r)$ and $n_y(r)$. The free-energy variation per unit volume is written as

$$\Delta F = \frac{1}{2V} \sum_{\vec{q}} K_1 [n_x(\vec{q}) q_x + n_y(\vec{q}) q_y]^2 + K_2 [n_x(\vec{q}) q_y - n_y(\vec{q}) q_x]^2 + (K_3 q_z^2 + \chi_a H^2)[n_x^2(\vec{q}) + n_y^2(\vec{q})] . \tag{4}$$

For a given $\vec{q}$ we can diagonalize this quadratic form by a linear transformation of the basis of the reference system: $(\vec{x}, \vec{y}, \vec{z}) \rightarrow (\vec{e}_1, \vec{e}_2, \vec{z})$; $\vec{e}_2$ being perpendicular to $\vec{q}$, with a transformation matrix

$$P = 1/(q_x^2 + q_y^2)^{1/2} \begin{pmatrix} q_x & -q_y \\ q_y & q_x \end{pmatrix} . \tag{5}$$

This leads to the following diagonal form:

$$\Delta F = \frac{1}{2V} \sum_{\vec{q}} \sum_{\alpha=1,2} n_\alpha^2(q) (K_\alpha q_\perp^2 + K_3 q_z^2 + \chi_a H^2) . \tag{6}$$

For each $\vec{q}$ value we have a mixture of two fluctuation modes schematically described in Fig. 4: mode $\alpha = 1$ is a mixture of splay and bend; mode $\alpha = 2$ is a mixture of twist and bend. The two modes are decoupled and one can use, in the classical limit, the theorem of equipartition of energy:

$$\langle |n_\alpha(q)|^2 \rangle = V k_B T / (K_\alpha q_\perp^2 + K_3 q_z^2 + \chi_a H^2) . \tag{7}$$

We finally get in real space

$$J = \langle n_x^2(r) + n_y^2(r) \rangle = \frac{k_B T}{(2\pi)^3} \int_{q_m}^{q_M} \left(\sum_{\alpha=1,2} (K_\alpha q_\perp^2 + K_3 q_z^2 + \chi_a H^2)^{-1} \right) d^3q . \tag{8}$$

The integral evaluated in the continuum limit diverges for $|q| \rightarrow \infty$; a higher cutoff must be introduced in the integral $q_M \sim 1/a$, where a is an intermolecular distance. The lower cutoff is given by the size of the sample (the thickness L of the cell in our experiments, with a nematic film contained between two parallel plates). It can be safely taken as $q_m = 0$ in the present calculation, which is of interest for fields much larger than the typical Freedericksz fields $H_{c,i}$ or, equivalently, when L is much larger than the magnetic correlation lengths $\xi_i = (K_i/\chi_a H^2)^{1/2}$ defined in the Appendix [formula (A7)]. The expression of J simplifies by using ξ_i and stretched momentums $(q'_{i\alpha})$

$$q'_x = q_x , \quad q'_y = q_y , \quad q'_z = (K_3/K_\alpha)^{1/2} q_z . \tag{9}$$

One obtains:

$$J = \frac{k_B T}{2\pi^2} \left(\frac{K_\alpha}{K_3} \right)^{1/2} \sum_{\alpha=1,2} \int_0^{q'_{\alpha M}} \frac{q'^2 dq'}{K_\alpha q'^2 + \chi_a H^2} , \tag{10}$$

$$J = \frac{k_B T}{2\pi^2 K_3^{1/2}} \sum_{\alpha=1,2} \frac{1}{K_\alpha^{1/2}} \left(q'_{\alpha M} - \frac{\pi}{2\xi_\alpha} \right) . \tag{11}$$

The reduction of the fluctuations by the magnetic field is easily understood from this last result. In the nematic state, in the absence of fields, there is no natural large correlation length and long wavelength fluctuations contribute up to the size of

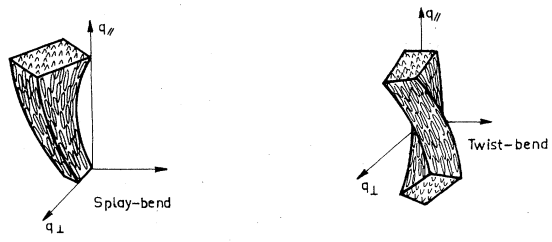

FIG. 4. Schematic representation of the mixed modes ($\alpha = 1, 2$) of the theoretical analysis. Near the smectic transition it is the divergence of the bend part which causes the vanishing of the IEB.

L. However, when the field is applied, a low-frequency cutoff $\pi/2\xi_i$ is introduced in the problem. Larger wavelength fluctuations are suppressed. This causes an increase of

$$\langle n_z^2\rangle = \langle 1 - n_x^2 - n_y^2\rangle = 1 - J, \tag{12}$$

which is proportional to the increase of the birefringence of the nematic:

$$\frac{\Delta n(H,T) - \Delta n(H=0,T)}{\Delta n_0} = \frac{\langle n_z^2(H)\rangle - \langle n_z^2(H=0)}{1}, \tag{13}$$

$$\frac{\Delta n(H,T) - \Delta n(H=0,T)}{\Delta n_0} = \frac{k_B T}{4\pi K_3^{1/2}}\left(\frac{1}{\xi_1(H)} + \frac{1}{\xi_2(H)}\right), \tag{14}$$

and, finally,

$$\frac{\Delta n(H,T) - \Delta n(H=0,T)}{\Delta n_0} = \frac{k_B T}{4\pi}\left(\frac{\chi_a}{K_3}\right)^{1/2} \times\left(\frac{1}{K1} + \frac{1}{K2}\right)|H| . \tag{15}$$

This formula is the central result of the study.

At this stage we can make several remarks about this formula: (i) The predicted effect is very small. Using $\chi_a \sim 10^{-7}$ cgs and $K_i \sim 10^{-6}$ cgs, one calculates $\delta(\Delta n)/\Delta n \sim 10^{-4}$ for $H = 10^5$ Oe. So very sensitive optical techniques as well as unusually large fields are required. (ii) Near a nematic-to-smectic second-order transition, the twist (K_2) and bend (K_3) elastic constants diverge, as discussed in the Appendix. This causes the quenching on the mixed modes ($\alpha = 1,2$). The IEB effect decays continuously to zero. (iii) On the other hand, the decrease of the elastic constants near the isotropic transition is faster ($\propto S^2$ in a mean-field model) than that of χ_a, proportional to S. So one expects an increase of the IEB as T_{NI} is approached from below.

The effect reported here corresponds, in a sense, to an "internal-field effect" where the magnetic field acts to suppress the large-scale variations of the distortion in a manner similar to the Freedericksz effect, where, in large fields, the distorsion is restricted to sheaths (next to boundaries) or to walls of extent comparable to ξ_i.

B. Magnetic analogy

The approach developed above is strongly analogous to the classical treatment of magnetic systems in a field. In an *isotropic* ferromagnet below the Curie point, the energy required to rotate the magnetization as a whole is zero, as it is the energy of long-wavelength spin-wave modes. Thus the transverse magnetic susceptibility measuring the ability of the magnetization to rotate in a small transverse field is infinite. If one assumes that the magnetic moment $\vec{M}$ rotates in the field without changing in amplitude (which is the basic assumption of this "semiclassical" approach) one can express a relation between the transverse and longitudinal fluctuations of $\vec{M}$ and calculate the increase of the longitudinal susceptibility due to the reduction of the transverse fluctuations in a field $\vec{H}$ parallel to $\vec{M}$. This approach was taken in particular by Vaks, Larkin, and Pikin[7] and its generality to a large class of multicomponent order-parameter systems was emphasized later by Patashinskii and Pokrovskii.[8]

Starting from the pioneering work of Brezin and Wallace[9] using renormalization-group arguments, several authors[10] have reconsidered the problem of the divergence of this longitudinal susceptibility and found it to vary as

$$H^{-\epsilon/2}, \quad (\epsilon = 4 - d),$$

for systems having different components of the order parameter. The result agrees with the semiclassical one. Thus these recent approaches can be considered as a justification of the fundamental assumption of the "semiclassical approach", i.e., the neglect of amplitude fluctuations of $\vec{M}$ in front of the angular (or phase) ones.

On the other hand, at the present time there seems to be no available experimental result on the subject. The main reason for this is the fact that the situation of "isotropic" magnetic systems cannot be produced in general; anisotropic magnetocrystalline effects are dominant in low fields—far from saturation—where the divergence should be seen. Theoretically, the absence of complete rotational symmetry leads to a quenching of the transverse fluctuations in low fields and to the suppression of the critical behavior.[10] Antiferromagnetic systems would be better candidates if measurements of the staggered magnetization were available. The nematic phase has the isotropic character required for the above approach. In large magnetic fields the anisotropic effect introduced by the orienting action of the walls is effective over a thickness $\xi_i(H)$, much smaller than the cell thickness, and can be neglected. In order to show the correspondence between the critical exponent $u = 1 \pm 0.02$ obtained here and the value of the exponent $-\frac{1}{2}\epsilon = -\frac{1}{2}$ of the longitudinal susceptibility, we present schematically a magnetic calculation paralleling that given above for the nematic case.

The magnetization is taken as having a constant modulus M_0 and $M_\parallel^2 + M_\perp^2 = M_0^2$ ($\parallel$ and $\perp$ defined with respect to the direction of $\vec{H}$). Thus $M_\parallel(H) \sim M_0 - \frac{1}{2}M_\perp^2/M_0$ (as $M_\perp$ is small in front of M_0). In momentum space,

$$M_{\parallel}(H) = M_0 - A \sum_q M_{1q}^2(H).$$

We can get the Fourier components of the transverse magnetization fluctuation from a linearized Landau free-energy expansion:

$$F = \sum_q (aH + q^2) M_{1q}^2 \quad (A \text{ and } a \text{ are constants}).$$

The first term connects with the divergence of $M_\perp$ as H^{-1}, whereas the second one is the usual gradient term. The factor can be written as $\xi^{-2} + q^2$, where the magnetic correlation length ξ varies as $H^{-1/2}$. The equipartition theorem applied to the normal modes of F gives $M_{1q}^2 = kT/(aH + q^2)$. If one replaces the summation by an integration in d dimensions and subtracts the finite value $M_{\parallel}(0)$ of the magnetization in zero field we get the increase of magnetization

$$\Delta M(H) = M_{\parallel}(H) - M_{\parallel}(0) \propto \int \frac{q^{d-1}dq}{q^2 + \xi^{-2}} - \int \frac{q^{d-1}dq}{q^2}$$

$$= \xi^{-2} \int \frac{q^{d-3}dq}{q^2 + \xi^{-2}} \propto \xi^{2-d} \propto H^{(d-2)/2}.$$

From this result the variation of

$$\chi_{\parallel}(H) = \frac{M_{\parallel}(H) - M_{\parallel}(0)}{H} \propto H^{(d-4)/2}$$

follows. The description extends directly in the nematic case if one replaces the dependence of ξ as $H^{-1/2}$ by H^{-1} (the change comes basically from the replacement of a magnetic energy MH by $\chi_a H^2$). Thus the IEB, which corresponds to the difference $\Delta M(H)$ in the magnetic problem, should vary as H^{d-2} with field. (The longitudinal susceptibility, which would be measured by the correlation function of the birefringence as two points along the field, would vary as H^{d-4}.) Thus the variation of the IEB as $H^{1\pm0.02}$ is not a trivial result but confirms the validity of the $d-2$ exponent variation and provides a first experimental verification of critical dependence of the magnetic-susceptibility fields.

III. EXPERIMENTAL

The experiments have been performed on (i) 4′-*n*-heptyl-4-cyanobiphenyl (7CB), C_7H_{15}-⟨φ⟩-⟨φ⟩-C≡N, which has a nematic phase with an order temperature $T_{NI} = 41.8\,^\circ\text{C}$ and no smectic phase; (ii) 4′-*n*-octyl-4-cyanobiphenyl (8CB) C_8H_{17}-⟨φ⟩-⟨φ⟩-C≡N, which presents both a smectic-*A* and a nematic phase, with critical temperatures $T_{AN} = 32.5\,^\circ\text{C}$ and $T_{NI} = 40.0\,^\circ\text{C}$. We have chosen these materials because they have a good chemical stability: The transition temperatures varied by less than $0.1\,^\circ\text{C}$ throughout the time of the experiments.

The nematic sample is contained within a calibrated cell (provided by the Hellma Society) of thickness $d = 200 \pm 5$ μm. The parallelism between the boundary plates is better than 10^{-4} rad. In order to realize a planar anchoring (the director $\vec{n}$ uniformly parallel to the plates), the inner sides of the two plates were first separately coated with an obliquely incident evaporated film of SiO,[11] and sealed together. The space between the two plates is optically controlled. The cell is then filled under vacuum with liquid crystals.

The polarimetry device used was developed by Maret.[12] The birefringence can be measured continuously using a photoelastic modulation technique and an automatically compensating Pockels cell. A resolution of $\Delta n \sim 10^{-7}$ is achieved for a 200 μm sample thickness at a wavelength $\lambda = 6328$ Å. The response time is shorter than 30 ms.

The magnetic field, variable between 0 and 1.5×10^5 Oe, is produced by a Bitter coil. The laser beam passes through the coil along the x direction, perpendicular to the magnetic field direction z (Fig. 5). The cell is positioned in such a way that the direction of the director $\vec{n}$ is parallel to that of the field. Thus the cell can be rotated by angular steps of 2′, around two rotation axes by means of a slow-motion mechanism as shown in Fig. 5. The angle β (rotation around y' axis), between the plane of the cell and the $\vec{H}$ direction, is brought to zero by realizing a coincidence between incident and reflected beams. The angle α (rotation around the laser-beam direction) between $\vec{n}$ and $\vec{H}$ can be adjusted to zero by suppressing the parasitic orientation effect in low fields (see Sec. IV B).

The large intrinsic birefringence of nematics in zero field is strongly temperature dependent: $\Delta n/\Delta T \sim 10^{-2}\,^\circ\text{C}^{-1}$.[13] This effect can be kept to less than 10^{-2} of the magnetic-field contribution by sta-

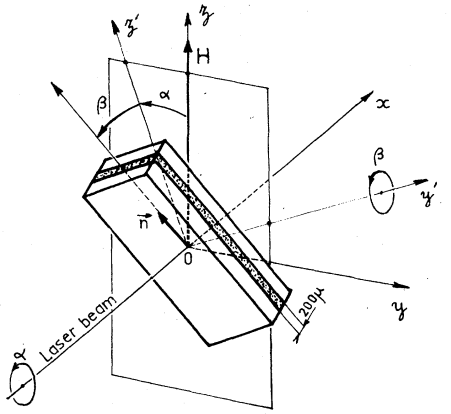

FIG. 5. Indication of the geometry of the nematic cell and the procedure of alignment around the two axes x and y' to bring the axis to the reference frame $0xyz$.

bilizing the temperature to 3×10^{-3} °C over the time of application of the field. We could not use an electronic stabilization: Magnetoresistive effects limit the use of resistor thermometers which would be the most sensitive in this temperature range; on the other hand, eddy-current effects strongly influence the functioning of electronic regulations. For these reasons we have used a stabilization by thermal inertia (large heat capacitance and poor thermal coupling with the surrounding). The sample is placed in a thick Teflon container surrounded by a cylindrical copper oven in which water, stabilized to better than 0.01 °C, circulates. This oven is insulated from the inner walls of the Bitter coil where the power dissipation is 5 MW. The variation of temperature is of the order of 3.10^{-3} °C over 10 min; the time of application of the magnetic field is approximately ten times smaller.

IV. EXPERIMENTAL RESULTS

A. Behavior of birefringence with magnetic field

An unretouched experimental variation of IEB versus magnetic field is given in Fig. 6 for an 8CB nematic sample (the thickness is 200 μm, the temperature is 37 °C). It represents the variation of the magnetically induced phase shift $\Delta\phi$, directly proportional to the voltage applied to the compensating Pockels cell, versus the magnetic field. In the same figure we have drawn variations $\Delta\phi = KH^u$ with different exponents u. Within the noise limitation we can state that the IEB $\delta(\Delta n)$ varies like H^u with an exponent $0.98 \leq u \leq 1.02$. This law of variation is obtained over the *entire* nematic range. It is drastically different from that obtained in the isotropic case, where the induced birefringence (Cotton-Mouton effect) varies as H^2.[14] On the other hand, in the smectic phase we observe no variations of birefringence with the applied magnetic field ($u = 0$). Another characteristic feature is the nonanalytic

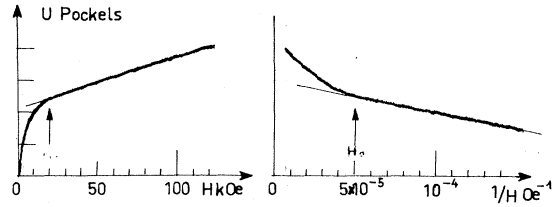

FIG. 7. Two plots of the same variation of the IEB with field indicating the existence of separate domains of variation for the alignment effect (linear in $1/H$) in a poorly aligned sample ($\alpha = 5°$) and for the IEB (linear with H). The arrow corresponds to a field $H = H_0 = 100\, H_c$ (see Fig. 13 and Appendix).

dependence as $|H|$. Indeed, we verify that by changing the direction of the magnetic field by 180° we get the same value of the birefringence. This result can be easily understood as coming from the symmetry $\vec{n} \rightarrow -\vec{n}$ of the nematic phase.

B. Alignment effect

Before further developing the implications of these results, let us consider the effect of alignment. In the experiment of Fig. 6 the direction of the molecular alignment was adjusted parallel to the magnetic field to better than 2′. A poor alignment of the sample in the magnetic field induces a parasitic phenomenon which is most visible in low fields. In Fig. 7 the variation of the birefringence with magnetic field is recorded for a misalignment angle $\alpha = 5°$, both as a function of H [Fig. 7(a)] and of $1/H$ [Fig. 7(b)].

In the Appendix, we show that the effect of a magnetic field on a poorly aligned sample should lead to an H^{-1} variation of the birefringence. The effect can be understood as coming from the contribution of two layers next to the limiting plates, of thickness $\xi(H) \propto H^{-1}$, which retain the alignment at the plates different from that of the field.

The curves of Fig. 7 clearly show that one can separate the effect of the field alignment of that of

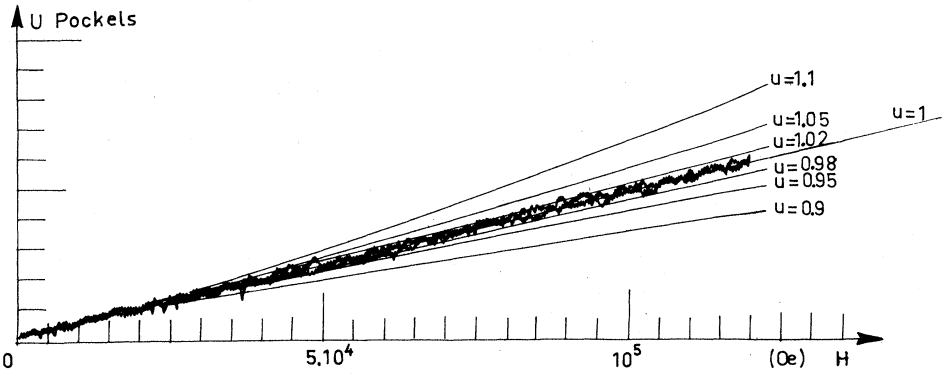

FIG. 6. Direct plot of the variation of Pockels-cell voltage (linear in the excess birefringence variation) with field. The scanning is obtained by increasing the field linearly with time and is reversible. The best fit is obtained for a variation of H^u with $u = 1 \pm 0.02$.

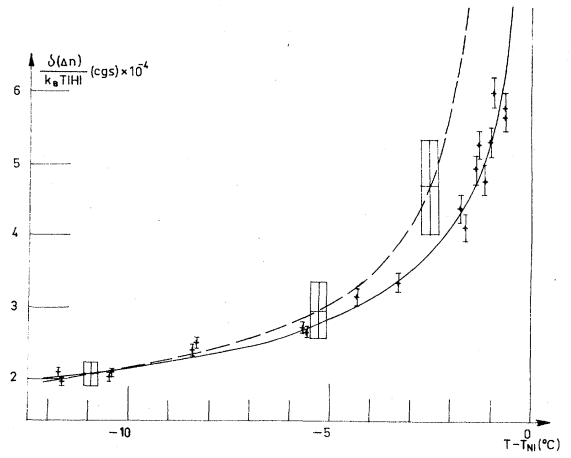

FIG. 8. Variation of IEB versus temperature in the nematic phase of 7CB. The full line represents the slope of high magnetic field measurements (see Fig. 6). The broken line is the calculated curve. The value of T_{NI} has been adjusted to coincide in both cases.

the IEB. In low fields the variation of birefringence is linear in H^{-1}, the dominant effect being the macroscopic alignment of the molecules along the magnetic-field direction. In high fields, the birefringence varies as H, as the dominant effect is due to the reduction of the fluctuations of orientation. The crossover between these two regimes takes place around 30 000 Oe for $\alpha = 5°$. The value agrees with a numerical evaluation based on formula (A6) of the Appendix.

C. Temperature dependence of the IEB

The linear variation of $\delta(\Delta n)$ with $|H|$, discussed in Sec. IV A for a 200-μm thick 8 CB sample at 37 °C, has been obtained[15] systematically for both 7CB and 8CB samples over their whole nematic temperature range. Figures 8 and 9 give the variations with temperature of the increase of the slope of the IEB, normalized to $k_B T|H|$, for 7CB and 8CB. In both cases, for a given field, the IEB increases drastically, near the nematic-isotropic transition. On the other hand, for 8CB the IEB decreases continuously to zero at the smectic-A–nematic transition temperature T_{AN}. These experimental results agree with theoretical predictions developed in Sec. II and discussed in the following paragraph.

D. Comparison with theory

Formula (15) indicates how the term $\delta(\Delta n)/k_B T$ depends on the three elastic constants and on the anisotropic susceptibility. It can be written as

$$A(T) = \frac{\delta(\Delta n)}{k_B T(H)} = \frac{\Delta n_0}{4\pi}\left(\frac{\chi_a}{K_3}\right)^{1/2}\left(\frac{1}{K_1}+\frac{1}{K_2}\right), \quad (16)$$

where Δn_0 represents the birefringence of a fully oriented sample, corresponding to an order pa-

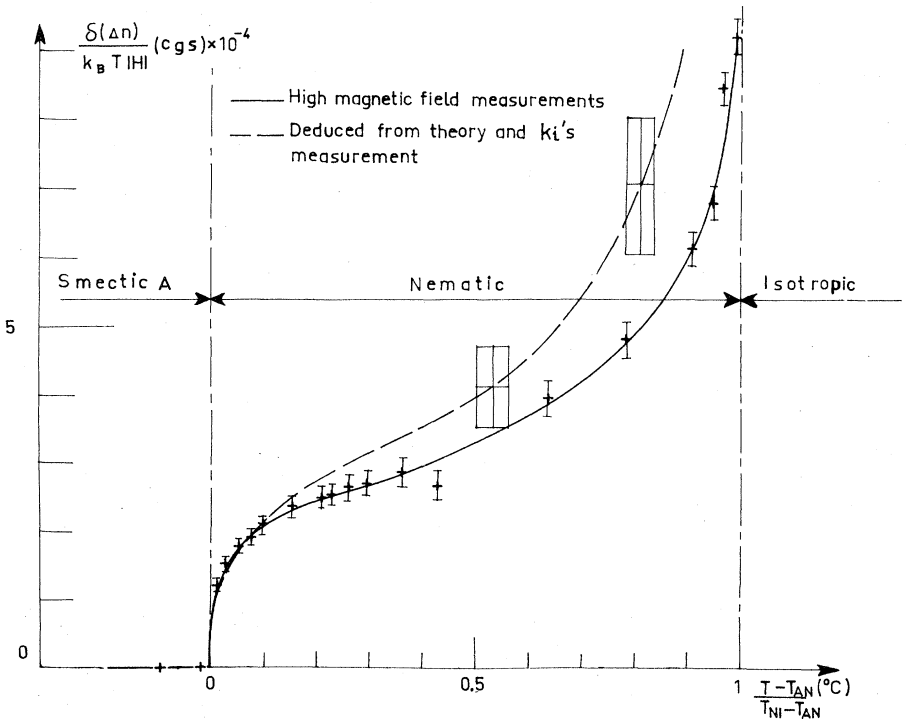

FIG. 9. Variation of the IEB versus temperature in the nematic phase of 8CB. The temperature has been normalized in order to adjust the transition temperature T_{AN} and T_{NI} between experimental and calculated curves.

rameter $S=1$. Thus $\Delta n=\Delta n_0/S=\Delta n\chi_{a0}/\chi_a$.[1] From the values of X_a and X_{a0}, given in Fig. 2, and of Δn (Refs. 16 and 17) we get $\Delta n_0=0.23$. Using formula (16) we have calculated the variation of the IEB through the nematic temperature range. The elastic constants were determined from Freedericksz' threshold measurements in conditions as close as possible to the IEB experiment, as reported in the Appendix. This precaution is important, as it has been often found that the value of K_i could depend markedly on the liquid-crystal preparation (residual impurities, conditioning, and handling).

A comparison between the calculated (broken line) and experimental IEB data is done in Figs. 8 and 9 for 7CB and 8CB. The relative uncertainty of the calculated value of $A(T)$ is due mostly to that of the K_i and is largest near T_{NI}, where it is 15%.

We can see that the experimental and theoretical variations are in good quantitative agreement over most of the nematic range.

(1) In the case of 8CB the approach of the second-order phase transition, leading to a freezing of the mixed elastic modes at low temperature, is well described by experiments and theory. The critical temperature T_{AN} can be obtained by an extrapolation of the slope $A(T)$ to zero. More precisely, we can evaluate the critical dependence of $A(T)$ near the second-order phase transition from that of the elastic constants K_i. One expects K_3 and K_2 to diverge as $(T-T_{AN})^{-\nu}$, where the exponents ν determined from various experiments[18,19] is compatible with the mean-field value $\nu=0.5$. It follows that $A(T)$ should vary as $(T-T_{AN})^{\nu/2}\sim(T-T_{AN})^{1/4}$; the experimental variation is compatible with such a variation. An extrapolation of the linear variation of $A(T)$ vs T^4 to zero leads to the determination of T_{AN} with an accuracy of 10^{-2} °C. We have no variation of T_{AN} within this accuracy when H varies from 0 to 120 kOe. Our results contradict data obtained by Rayleigh scattering and reported in Ref. 20 which indicated that a magnetic field of 700 Oe shifts the transition temperature T_{AN} of EMBAC liquid crystal by 1 °C.

Note. The quenching of the transverse fluctuations of orientation at the smectic transition is reminiscent of the Higgs mechanism,[21] much discussed in elementary-particle theory. This is the situation of a phase transition where the order parameter is coupled to a gauge field, the canonical example in condensed matter physics being the superconducting transition (in this case the gauge field is the electromagnetic field and the coupling occurs because the Cooper pairs are electrically charged). The Higgs mechanism proper consists of the fact that the electromagnetic field, purely transverse (zero-mass photon) in the normal phase, becomes an impurely transverse (massive) vector field in the superconducting phase, via coupling with the phase of the order parameter. Thereby we have the Meissner effect, finite penetration of the magnetic field in a superconductor, understood as due to the finite mass of the photon (expressible in terms of the London penetration length). As first noted by de Gennes,[31] a limited analogy exists in the case of the nematic–smectic-A transition, where the smectic order parameter (which has an amplitude and a phase) is the analog of the superconducting order parameter, and where the nematic director field is somewhat the analog of the electromagnetic gauge field. The transverse fluctuations of orientation are important in the nematic phase (they are massless) and quenched in the smectic phase (they are massive). This is just a commentary on the form taken by the denominator of Eq. (7) for $n_\alpha(q)^2$ in the limit q and $H\to 0$.

(2) The agreement is not so good near the nematic-isotropic transition although the temperature has been adjusted to the value of T_{NI} (which is determined as the temperature where the intrinsic birefringence jumps suddenly to zero).

A possible explanation would be that the nature of the transition to the isotropic phase is modified in the presence of large fields. In magnetic systems the second-order transition taking place at the Curie temperature T_c is replaced by a continuous variation which is described by a universal equation of state expressing the width of the transition region in $T-T_c$ as a function of the applied magnetic field H.[9] On the other hand, right at T_c the equation of state expresses H varying as M^δ, where the exponent δ characterizes the divergence of the susceptibility at T_c ($\chi\propto H^{1/\delta-1}$), which gives a variation of M between that in the disordered and ordered phase.

(3) In the present experiments we observe a large deviation of the variation of $A(T)$ near T_{NI} from the semiclassical model discussed above (approximately by a factor of 1.5 at $T_{NI}-1°$). However, we have found no variation of $A(T)$ nor of T_{NI} with the field within the accuracy of the experiments. Similarly the variation of the IEB with the field does not show any variation from the linear form, up to the highest temperature studied ($T=T_{NI}-5\times10^{-2}$). This suggests that the discrepancy observed is not directly connected with a "magneticlike crossover," which is not surprising because the experiments in the nematic phase are not close to the conditions of a vanishing order parameter but show a discontinuous transition. This result is justified by a rough estimate of the crossover field for the nematic-isotropic transition: The linearized form of the rate of variation of the free energy near T_{NI} can be written in a Landau

model[23] as

$$\frac{\partial F}{\partial T} = aS^2 \simeq 10^{-1} S^2 \simeq 10^{-2}\ \mathrm{J\ cm^{-3}\ °C^{-1}}.$$

If we compare this term with the magnetic anisotropy term $\chi_a H^2$ ($\chi_a \simeq 10^{-7}$ cgs) we expect that a value of 10^5 Oe would induce a change of T_{NI} of the order 10^{-2} °C (10^6 Oe for 1 °C) too small to be observed in the present experiments.

In fact, the approach of the nematic-isotropic transition has not yet received a satisfactory description. On the one hand, the variations of the elastic constants or of the susceptibility do not follow the mean-field description well as the transition is approached from below.[24] Another finding of Ref. 24 discussed separately[25] is that the mean-field approach does not apply well when T_{NI} is approached from above. In Ref. 14 it had been found that the inverse of the Cotton-Mouton constants, as well as the Kerr constants, measuring the ratio between the induced birefringence and the square of the magnetic or electric field above T_{NI}, varied linearly with temperature, extrapolating to a second-order transition temperature T^* slightly below the weakly-first-order nematic-isotropic transition (small latent heat) at T_{NI}: $T^* \sim T_{NI} - 1°$. Thanks to the greater accuracy of the present optical experiments we have shown[25] that a systematic deviation from the linear variation is observed in a temperature range of a few degrees above T_{NI}, qualitatively similar to that of the magnetic susceptibility above the Curie point and due to critical effects. A similar variation is shown in Fig. 2 of the recent letter by Keyes and Shane[26] although no explanation is proposed. Rather than emphasize the role of a tricritical point (which would justify the existence of normal exponents rather than critical ones), one may try to analyze the deviations from linearity observed in the three different studies as an indication of the onset of critical effects around T^*.

V. CONCLUSION

We have studied the quenching of the fluctuations of orientation by magnetic field over the whole temperature range of nematics. The linear dependence of induced excess birefringence IEB upon magnetic field has the same physical origin as the $H^{-\epsilon/2}$ behavior of the longitudinal susceptibility in magnetic systems discussed in Ref. 8 and is due to the freezing of angular fluctuations of the order parameter. In this respect the present experiments can be considered as a first experimental evidence of this critical behavior. The decrease of the IEB near a second-order transition to a smectic phase is quantitatively consistent with the freezing of the bend and twist elastic modes. The increase of IEB near the nematic-isotropic transition is due to a decrease of the elasticity. Deviations observed near this transition suggest the need for a description of this critical point; deviations from Kerr and Cotton-Mouton constants from the mean-field behavior also indicate the need for a better description of the first-order nematic-isotropic transition. Recent contributions[26] suggest that the transition temperature T^* is a tricritical point which would justify the applicability of mean-field exponents also obtained in the de Gennes-Landau approach. However, the present results indicate deviations from this model. Experimentally, one may think of approaching the mestastable second-order transition at T^* using dynamic experiments. The recent discovery of discocyte nematics[27] of negative order parameters also suggests the possibility of using a mixture of platelike and cigarlike molecules [the first-order transition is connected to the different nature of the states characterized by positive and negative values of $S(\vec{r})$ defined in Eq. (1)] which would undergo a second-order isotropic transition.

Note added in proof. We have just received a paper from Blinov on the reductions of fluctuations in cholesterics [S. V. Belayev, L. M. Blinov, and V. A. Kizel, Pis'ma Zh. Eksp. Th. Fiz. 29, 17 (1979)]. Their experiments measuring the variations of the selective reflection band of a cholesteric in an external electric field should be connected with IEB effect.

ACKNOWLEDGMENTS

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APPENDIX

The Freedericksz transition,[28] or "field effect," describes the distortion of a nematic film, initially aligned by wall effects, by a magnetic field. The effect of alignment along the field is described by the existence of an anisotropic magnetic susceptibility. In its most classical form, the single-crystal nematic sample is contained in a parallel wall cell of thickness d. The planar (director $\vec{n}$ parallel to the walls) or homeotropic ($\vec{n}$ perpendicular to the walls) alignment is obtained by suitable surface treatment.[11,29] The distortion pattern can be calculated from the minimization of the total free energy.

$$F = F_{mag} + F_{el}, \tag{A1}$$

where the magnetic contribution expressing the

tendency of alignment along the field is

$$F_{\text{mag}} = -\tfrac{1}{2}\chi_a(\vec{n}\cdot\vec{H})^2 d^3r. \qquad \text{(A2)}$$

The Frank elastic free energy is

$$F_{\text{el}} = \frac{1}{2}\int (K_1(\text{div}\,\vec{n})^2 + K_2(\vec{n}\cdot r\vec{o}t\vec{n})^2 + K_3(\vec{n}\times r\vec{o}t\vec{n})^2)\, d^3r. \qquad \text{(A3)}$$

The elastic deformations are described by the elastic constants K_1 (splay), K_2(twist), and K_3 (bend) (Fig. 3). Appropriate boundary conditions on $\vec{n}$ must be also expressed. In the case discussed below, where strong anchoring is assumed, the conditions reduce to $\vec{n}=\vec{n}_{\text{bound}}=\text{const}$.

A. Elastic-constants determination

If the field is perpendicular to the unperturbed alignment, the distortion takes place only above a critical field

$$H_{ci} = (K_i/\chi_a)^{1/2} d^{-1}, \qquad \text{(A4)}$$

where the index i refers to the three geometries described in Fig. 3. Right above the threshold H_{ci}, the infinitesimal distortion in case i is characterized by only one of the three elementary Frank elastic constants K_i.

However, above H_{ci}, a mixture of K_1 and K_3 distortions describe the rate of increase of distortion in the case of geometries 1 and 3.

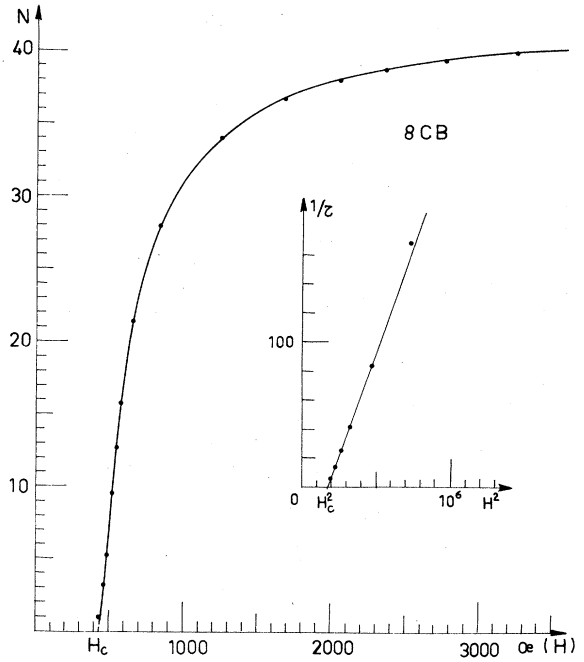

FIG. 10. Measurement of the threshold field of the Freedericksz transition obtained by extrapolating the variation of birefringence with field to zero (static effect). Inset: measurement obtained by measuring the relaxation time of the transition (dynamic effect).

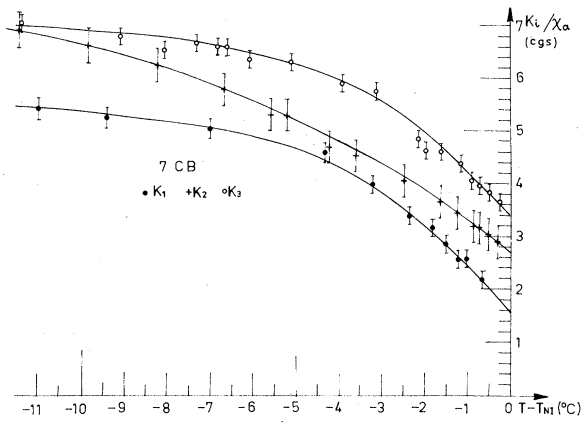

FIG. 11. Variation of K_i/χ_a of 7CB versus temperature obtained from the Freedericksz transition measurements.

The definition of the elastic constants can be understood directly from the image of the distortion just above threshold in the three geometries of Fig. 3. It is also indicated schematically, in the same figure, in a manner pictorially similar to the mixed modes given in Fig. 4. The measurement of the threshold magnetic fields H_{ci} has been applied to the evaluation of the three constants $K_i(T)$ in 7CB and 8CB, on which the IEB effect has been studied. The procedure is as follows

(i) The distortion is measured according to classical techniques: In geometry 1 and 3 we measure the variation of birefringence by counting the number of fringes produced in a nematic slab, placed between crossed polarizers at 45° with the director axis in geometry 1, in parallel monochromatic light. In geometry 2, the twist of the director is obtained from the rotation of the conoscopic image obtained in converging light.[30]

(ii) The critical field H_{ci} can be obtained from the extrapolation of the distortion to zero. A more sensitive measurement of H_{ci} uses the divergence of the relaxation time of the distortion

$$\rho(H) \propto [(H/H_{ci})^2 - 1]^{-1}, \qquad \text{(A5)}$$

when the field $H_{\text{init}} > H_{ci}$ is reduced to a value of the field $H < H_{ci}$.[31] The divergence is characteristic of the second-order phaselike transition at H_{ci}.

In Fig. 10 we indicate both types of determination of the critical field in the case of a planar sample ($d = 200$ μm). Using formula (A4) we get the temperature dependence of K_i/χ_a for the three elastic constants of 7CB and 8CB. The variations are given in Figs. 11 and 12. The results for 8CB clearly indicate the divergence of the twist and bend elastic constants at T_{AN}.

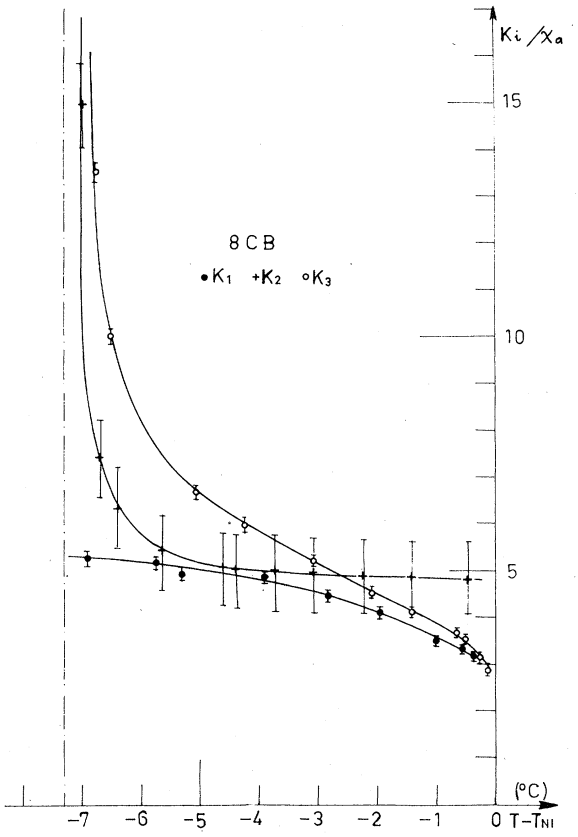

FIG. 12. Variation of K_i/χ_a of 8CB versus temperature obtained from Freedericksz transition measurements. Note the divergence of both K_2 and K_3 when approaching the smectic-A–nematic transition, while K_1 remains continuous.

(iii) The values of χ_a of 7CB[32] and 8CB,[33] known from direct susceptibility measurements, are given in Fig. 2.

(iv) Using the values of χ_a and those of K_i/χ_a the temperature dependence of the three elastic constants $K_i(T)$ is obtained for 7CB and 8CB.

From the temperature variation of the elastic constants and susceptibility one can deduce several features already reported in the literature which we recall briefly:

(a) Near T_{NI} the elastic constants and χ_a decrease. According to the Maier-Saupe molecular theory[34] one expects a variation of χ_a and K_i, respectively, as the order parameter S and as S^2. The ratio K_i/χ_a, measured by the critical field H_{ci}, must decrease as S when the temperature approaches T_{NI}. However, in this range of T deviations from the "mean-field" variation, already reported,[35] are also observed in the present experiments.

(b) On 8CB, which has a second-order phase transition to the smectic phase, the splay constant K_1 remains regular whereas both twist (K_2) and bend (K_3) constants diverge. In the smectic phase the presence of incompressible layers prevents the existence of the two latter types of distortion. In the pretransitional state one can understand the singular behavior as coming from the increasing role of fluctuating smectic domains (cybotactic groups). Considerable attention has been given to the critical indices characterizing such divergences.[18,19] No particular attention has been given to the form of the divergence in the present study but the existence of the critical behavior is reflected in the continuous freezing of the IEB (Sec. IV D) as T_{AN} is approached from above.

(c) The values of $K_i(T)$ are used in a quantitative comparison of the IEB results with the model in Sec. II. Let us note that our results on $K_i(T)$ are smaller by a factor of 2 than the measurements by Karat[16] on the same compound. However, Karat's experiments did not use any direct measurements of χ_a which were deduced from the susceptibility of the aromatic part of the molecule.[36]

B. Distortion induced by "poor" alignment between magnetic field and director

In connection with the present project, several years ago we had considered the problem of the alignment of a nematic slab by a magnetic field nearly parallel to the optical axis of a planar nematic.[37] The geometry is given in Fig. 13; α is the angle between the field $\vec{H}$ and the director $\vec{n}$ in the undistorted state.

In the usual Freedericksz problem there exists a symmetry which is broken by the distortion (in particular, this causes the existence of walls in the sample, comparable to magnetic walls, separating domains of symmetric angular distortion). The existence of a symmetry broken by the transition is closely connected with the second-order character of the phase transition.

In the present problem no symmetry is broken in the field; the distortion appears continuously as soon as a field is applied. The distortion[37] is plotted in Fig. 13. In reduced units ϕ, the birefringence effect integrated across the sample thickness is proportional to both the thickness d and the square of the angle α.

The major part of the alignment effect takes place around a value of the field of the order of a typical critical field $H_c = (K/\chi_a)^{1/2} d^{-1} \sim 300$ Oe for $d = 200$ μm (a one-elastic-constant approximation $K_i = K$ was assumed).

For large fields, ϕ saturates to a value ϕ_∞ corresponding to the alignment of $\vec{n}$ everywhere parallel to H with the following law:

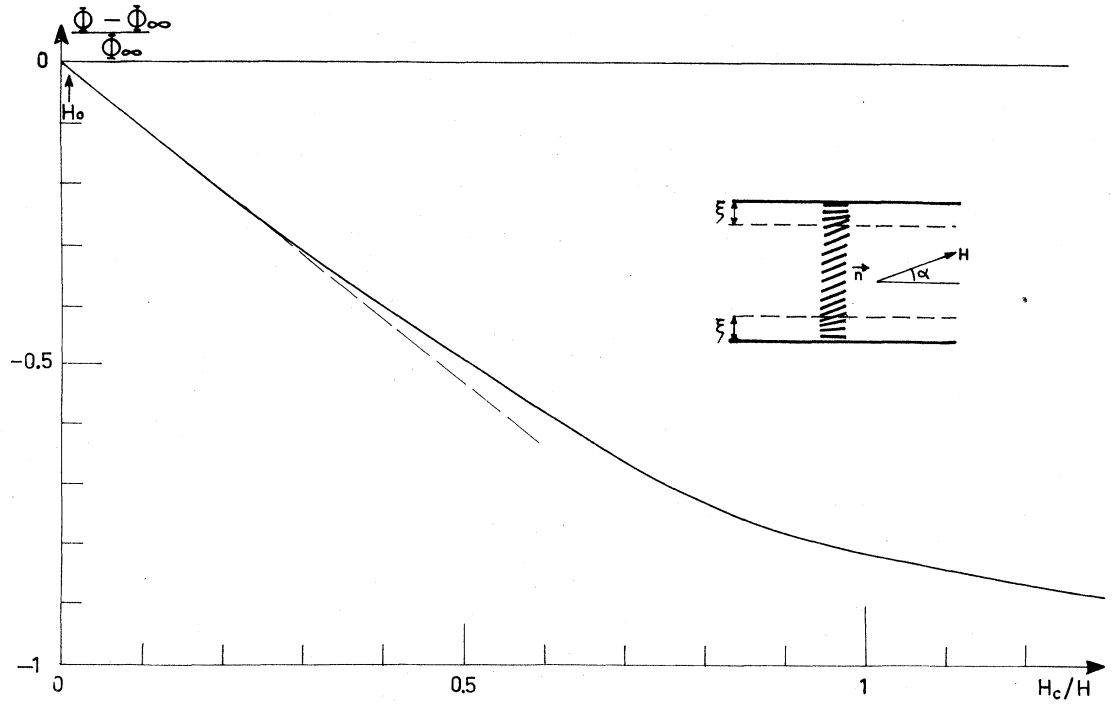

FIG. 13. Variation of the birefringence with magnetic field in the case of the nematic sample aligned initially at an angle α with H. The inset shows the existence of two boundary sheathes. H_0 refers to the value of the field indicated in Fig. 7.

$$\phi_\infty - \phi = \frac{3(n_e - n_0)\alpha^2 d}{H}\left(\frac{K}{\chi_a}\right)^{1/2}. \qquad \text{(A6)}$$

The formula reads easily: In the presence of a magnetic field a correlation length

$$\xi = (K/\chi_a)^{1/2} H^{-1} \qquad \text{(A7)}$$

is introduced, which is the length over which the alignment adjusts from the boundary value to the direction of H in the bulk.

The residual distortion $(\phi_\infty - \phi)$ is that of two superficial sheaths of thickness ξ with $\tilde{n}$ at an angle of the order of α with the field direction (Fig. 13, inset).

The notion of the magnetic correlation length is crucial in the present IEB study as ξ gives the upper limit of the wave vector of the possible spontaneous distortions of the director. Fluctuations of wave vector q larger than ξ^{-1} are energetically unfavorable.

Similarly, in the Freedericksz problem (Appendix A) the critical field H_{ci} could be expressed simply by stating that, for $H = H_{ci}$, the correlation length takes a value of the order of $d = \pi\xi(H_{ci})$.

[1]Y. Poggi, R. Aleonard and J. Robert, Phys. Lett. A 54, 393 (1975).
[2]A. de Vries, Mol. Cryst. Liq. Cryst. 10, 31 (1970); Acta Crystallogr. Sect. A 25, 5135 (1969).
[3]P. G. de Gennes, C. R. Acad. Sci. Ser. B 266, 15 (1968); see also *The Physics of Liquid Crystals* (Clarendon, Oxford, 1973), p. 110.
[4]Y. Poggi and J. C. Filippini, Phys. Rev. Lett. 39, 150 (1977).
[5]P. Chatelain, Acta Crystallogr. 1, 315 (1948).
[6]Orsay Liquid Crystal Group, Phys. Rev. Lett. 22, 1361 (1969).
[7]V. G. Vaks, A. I. Larkin, and S. A. Pikin, Sov. Phys.-JETP 26, 647 (1968).
[8]A. Z. Patashinskii and V. I. Pokrovskii, Sov. Phys.-JETP 37, 733 (1973).
[9]E. Brezin and D. J. Wallace, Phys. Rev. B 7, 1967 (1973).
[10]D. Nelson, Phys. Rev. B 13, 2222 (1976). (This recent approach of the problem contains an extended list of theoretical references on the subject.)
[11]W. Urbach, M. Boix, and E. Guyon, Appl. Phys. Lett. 25, 479 (1974).
[12]G. Maret and K. Dransfeld, Physica (Utrecht) 86.88

B + C, 1077 (1977).
[13]M. Brunet-Germain, C. R. Acad. Sci. Ser. B 271, 1075 (1970).
[14]T. N. Stinson and J. D. Litster, Phys. Rev. Lett. 25, 503 (1970); see also J. C. Filippini, Y. Poggi, and G. Maret, in *Colloque International du CNRS, physique sous champs magnetiques intenses* (CNRS, Paris, 1974).
[15]B. Malraison, C. R. Acad. Sci. Ser. B. 286, 307 (1978).
[16]P. P. Karat and N. V. Madhusudana, Mol. Cryst. Liq. Cryst. 36, 51 (1976); 40, 239 (1977).
[17]R. G. Horn, J. Phys. (Paris) 39, 105 (1978).
[18]P. E. Cladis, Phys. Rev. Lett. 31, 1200 (1973).
[19]M. Delaye, J. Phys. (Paris) Colloq. C3 37, C3 99 (1976).
[20]A. Sakamoto, K. Yoshino, V. Kubo, and Y. Invishi, Japan J. Appl. Phys. 15, 545 (1976).
[21]P. W. Higgs, Phys. Rev. Lett. 13, 508 (1964); E. S. Abers and B. W. Lee, Phys. Rep. 9C, 1 (1973).
[22]P. G. de Gennes, Solid State Commun. 10, 753 (1972).
[23]Y. Poggi, J. C. Filippini, and R. Aleonard, Phys. Lett. A 57, 53 (1976).
[24]B. Malraison, 3rd. cycle thesis, Université de Grenoble, 1978 (unpublished).
[25]B. Malraison, Y. Poggi, and J. C. Filippini, Solid State Commun. 31, 843 (1979).
[26]P. H. Keyes and J. R. Shane, Phys. Rev. Lett. 42, 722 (1979).
[27]S. Chandrasekar, B. K. Sadashiva, and K. A. Suresh, Pramana 9, 471 (1977); J. Billard, J. C. Dubois, Nguyen Huu Tinh, A. Zann, Nuovo J. Chim. 2, 535 (1978).
[28]See, for instance, H. J. Deuling, Solid State Phys. Suppl. 14 (1978).
[29]Homeotropic anchorage was obtained by lecithine coating. [P. Pieranski (private communication).]
[30]P. E. Cladis, Phys. Rev. Lett. 28, 1629 (1972).
[31]F. Brochard, P. Pieranski, and E. Guyon, Phys. Rev. Lett. 26, 1681 (1972).
[32]Y. Poggi, thesis, Université de Grenoble, 1977 (unpublished).
[33]We are indebted to Mme. Achard who made the measurement of χ_a on 8CB.
[34]W. Maier and A. Saupe, Z. Naturforsch. Teil A. 15, 237 (1960); J. Nehring and A. Saupe, J. Chem. Phys. 56, 5527 (1972).
[35]H. Gruler, Z. Naturforsch. Teil A. 28, 474 (1973); F. H. Leenhouts, F. Van der Woude, and A. J. Decker, Phys. Lett. A 58, 242 (1976).
[36]K. Lansdale, Rep. Prog. Phys. 4, 368 (1937).
[37]B. Malraison, P. Pieranski, and E. Guyon, J. Phys. Lett. (Paris) 35, 9 (1974).