Observation of Macroscopic Collective Behavior and New Texture in Magnetically Doped Liquid Crystals

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The observation of macroscopic collective behavior in a nematic liquid crystal doped with magnetic grains is reported. This behavior is manifested as a uniform molecular orientational distortion of the entire matrix upon the application of external magnetic fields as low as <1 G. The dependence of the distortion on field strength, dopant concentration, and sample thickness is presented, and a theory which quantitatively accounts for the results is given. At high field intensities, the doped nematic exhibits a heretofore unreported texture of complex cellular topology.

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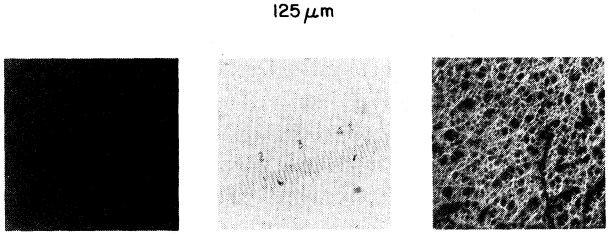
A distinctive characteristic of liquid crystals is the anisotropic nature of their physical properties. This anisotropy is manifested in the anisotropic response these materials exhibit upon the application of external fields. The study of the effects of applied electric fields has contributed significantly to our understanding of the physics of liquid crystals and laid the foundation for many of their technological applications. To obtain analogous effects with magnetic fields, high-field intensities ($\geq 10^3$ G) are required in order to overcome the typically minute anisotropy of the diamagnetic susceptibility ($\Delta\chi \simeq 10^{-7}$ cgs units) of liquid crystals. To circumvent this limitation, Brochard and de Gennes proposed "doping" the liquid crystal matrix with ferromagnetic grains.[1] In principle, this should make possible the coupling of the liquid-crystalline molecular orientation to weak external magnetic fields. These authors treated such a system theoretically and made the prediction that, at a critical concentration of well dispersed magnetic particles, the doped matrix should exhibit collective orientational distortion with an instability threshold occurring at a critical field value. They also predicted that the coupling between the magnetic particles and the liquid crystal molecules, which is mechanical in nature, would result in a matrix with ferromagnetic behavior [$M(H=0)\neq 0$].

Several attempts have been made at realizing this system experimentally.[2-4] However, in none of these experiments was the predicted collective behavior of the doped matrix achieved. The magnetic particles used were flocculated large clumps made of many grains which cluster as a result of magnetic interaction. Consequently, homogeneous distribution of the individual magnetic grains in the liquid crystal matrix was not attained. We report here what we believe to be the first observation of macroscopic collective behavior of a magnetically doped nematic liquid crystal.[5] The collective behavior is exhibited as a long-range uniform distortion of the molecular orientation of the entire sample upon the application of an external magnetic field as weak as <1 G [Figs. 1(a) and 1(b)]. A second new result is that at higher fields, the orientational distortion ceases to be uniform and is replaced by a new field-induced "cellular" texture, with the "cells" having dimensions on the order of tens of micrometers [Fig. 1(c)].

As will be shown below, we have experimentally determined that the magnetic grain is coupled to the nematic matrix such that its magnetic dipole moment is perpendicular to local nematic director n. Given this relative alignment, we treat the case of homeotropic alignment first [Fig. 2(a)].

For small molecular orientational distortion ($\Theta_M \ll 1$), the free energy of the system can be written in the following form:

$$F = \int_{-D/2}^{D/2} dz \left\{ \tfrac{1}{2} k_{33}(1 + K \sin^2\Theta)(d\Theta/dz)^2 - MH \sin\Theta(z) \right\}, \quad (1)$$



(a) H=0 (b) H=10G (c) H=30G

FIG. 1. Magnetically doped, homeotropically aligned nematic matrix viewed with polarizing microscope: (a) no field; (b) uniform field-induced birefringence; (c) "cellular" texture.

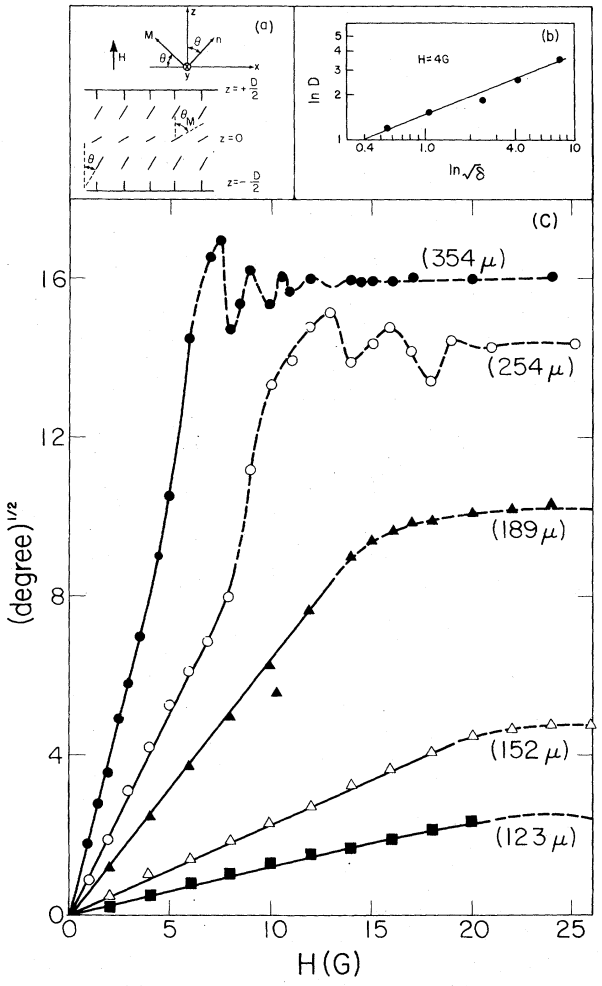


FIG. 2. (a) The molecular geometry; (b) the phase-difference dependence on sample thickness, $\delta \propto D^5$ as predicted by Eq. (4); (c) δ as a function of H for various thicknesses; filling factor = $16f$.

where $K=(k_{11}-k_{33})/k_{33}$; k_{11} and k_{33} are the splay and bend elastic constants, respectively; M is the matrix magnetization; H is the strength of the externally applied magnetic field.

By minimizing the free energy using the Euler-Lagrange equation, one can readily show that

$$d^2\Theta/dz^2+\xi^{-2}=0,$$

where

$$\xi=[k_{33}/MH]^{1/2}.$$

When we take the boundary conditions shown in Fig. 2(a) into consideration, then

$$\Theta(z)=\tfrac{1}{2}\xi^{-2}[(D/2)^2-z^2], \quad (2)$$

where D is the matrix thickness, and

$$\Theta_M=(MH/8k_{33})D^2. \quad (3)$$

The field-induced distortion of the doped matrix can be probed by measuring the corresponding induced change in birefringence. For small distortion $\Theta_M \ll 1$, it can be shown that the change in phase differences δ is given by[6]

$$\delta=(2\pi/\lambda)[\tfrac{8}{15}D^5(n_e-n_o)(M/8k_{33})^2]H^2, \quad (4)$$

where n_e and n_o are the extraordinary and ordinary indices of refraction of the nematic, respectively, and λ is the wavelength of the light used to measure the birefringence change.

In the case of homogeneous alignment, by following the steps outlined above one can readily show that for $\Theta_M \ll 1$

$$\Theta_M=(MH/8k_{11})D^2, \quad (5)$$

and that the phase difference is given by

$$\delta=(2\pi/\lambda)[\tfrac{8}{15}D^5(n_e-n_o)(M/8k_{11})^2]H^2. \quad (6)$$

The nematic liquid crystal used for this work was methoxybenzyledene butylanilne (MBBA). Homeotropic alignment was obtained by coating glass substrate with dimethyl octadecyl aminopropyl trimethoxysilyl chloride (DMOAP), while the homogeneous alignment was achieved by evaporating SiO on the substrate. The magnetic particles were γ-Fe_2O_3 needles 0.5 μm long and had an aspect ratio of ~ 7:1. Their magnetic dipole moment pointed along the long axis of the particle and was 70 emu/g. To prevent clumping, these needles were coated with DMOAP.[7] The distortion induced by the external magnetic field was measured as a change in the phase difference of the ordinary and extraordinary rays.[8] The sample was prepared by multiples of a basic (unity) filling factor[1] of the magnetic particles: 1.86×10^{-7} and 2.66×10^{-6} for the homeotropic and homogeneous alignments, respectively. For the homeotropic (homeogeneous) alignment, the magnetic dipole moment of the ferronematic matrix was first aligned by a weak (< 1 G) horizontal (vertical) field. The external field was applied with a pair of Helmholtz coils such that $H \| n$ for both alignments.

Experimental evidence for collective behavior —When observed between the crossed polarizers of a polarizing microscope, and upon the application of a weak external magnetic field ($H \leq 20$ G) such that $H \| n$, the entire doped matrix exhibited strong uniform birefringence as shown in Fig. 1(b). This effect was independent of the polarity of the applied field. That the entire sample (typically 0.5 cm across) became birefringent is evidence for collective behavior and indicative that

indeed single magnetic particles were homogeneously dispersed throughout the homeotropic nematic. The response time constant is typically on the order of 1–2 min. On the other hand, when the external field was applied perpendicular to the nematic director, no birefringence was observed, i.e., the field of view remained dark. Only when the strength of the applied field reached the critical field for *undoped* MBBA (≥ 200 G) did birefringence occur. The above results lead us to conclude that the magnetic particles, and consequently their dipole moments, lie perpendicular to the nematic director, which is consistent with the anchoring expected from DMOAP coating.

In cases where the concentration of the magnetic particles in the nematic matrix was high or when the particles were poorly coated, clumping occurred yielding anisotropic chains ~ 50 μm long. Once the clumping occurs, the collective behavior no longer takes place and the long-range orientational distortion is replaced by localized domains of birefringence limited spatially to the immediate vicinity of the individual clumps. Not unlike the case of singly dispersed particles, when the external field was perpendicular to n, no birefringence was observed. Upon rotation of the field in the horizontal plane, while maintaining the condition $H \perp n$, transient birefringence was observed as a halo surrounding the edge of the clump and was coherent with the motion of the rotating field. Identical results were obtained with the homogeneous alignment.

Distortion dependence on external magnetic field.—To gain a quantitative insight into the physics responsible for the observed orientational distortion, we studied the dependence of the field-induced birefringence on the strength of the applied field, the concentration of the magnetic dopant, and the thickness of the nematic matrix. The experimental results for the homeotropic alignment are shown in Figs. 2 and 3. A general feature of the dependence of δ on H is that the curves can be divided into two regimes: (1) At low fields, there is a regime where δ, which is a measure of the nematic orientational distortion, varies monotonically with the strength of the applied field. Equation (4) predicts that $\delta \propto H^2$. As can be seen, for small distortions, the measured phase difference δ is indeed proportional to the square of the applied field. No critical field was observed. A second prediction of Eq. (4) is that the phase difference is proportional to the square of the matrix magnetization M. This was

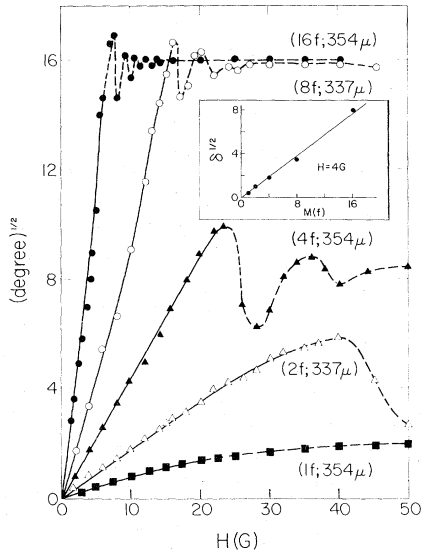


FIG. 3. Phase difference vs field strength for various magnetic dopant concentrations. Inset shows $\delta \propto M^2$ as predicted by Eq. (4).

tested experimentally by varying the concentration of the magnetic grains. The results are shown in Fig. 3 and are in excellent agreement with the theoretical predictions. Finally, the theory predicts that $\delta \propto D^5$. Again, for small distortion, the experimental results agree remarkably well with this prediction. (2) At higher fields, as the magnetic grains begin to flocculate into clumps, a saturation regime is reached where the δ dependence on H saturates in an oscillatory fashion. By examination with a polarizing microscope, we find that the onset of this regime corresponds to the transformation of the nematic matrix from a uniformly birefringent state into a complex texture with a "cellular" topology as seen in Fig. 1(c). The texture response time to the application or removal of the magnetic field is < 1 sec. We tentatively ascribe this texture to a nonuniform distortion of the molecular orientation whose spatial geometry is analogous to that observed in the case of Williams domains.[9] Identical results were obtained in the case of homogeneous alignment: For small orientational distortion, the behavior of the doped matrix is excellently described by Eq. (6); while at higher fields, δ saturates and the "cellular" texture is observed.

In summary, collective long-range orientational distortion of molecular order has been achieved in nematic matrix lightly doped with well dispersed magnetic needles. The fields required to obtain this macroscopic response are as low as

<1 G. At higher fields, as the magnetic particles clump into aggregates, a new liquid-crystalline texture is observed which has a cellular structure heretofore unreported in the literature.

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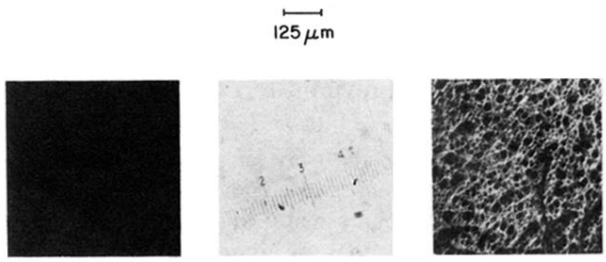

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