Nematic-Isotropic Transition: Thermal Hysteresis and Magnetic Field Effects

T. Riste and L. Dobrzynski*
Institutt for Energiteknikk, P.O. Box 40, N-2007 Kjeller, Norway

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Using neutron scattering, we have studied the effect of an applied magnetic field on the nematic-isotropic transition temperature T_c in para-azoxy-anisole (PAA). We have, for the first time, been able to measure a thermal hysteresis width, $(T_+^* - T_-^*)/T_c$, and find a value 3.7×10^{-4} for a field-aligned sample, much lower than any previous estimate, and decreasing to zero for weaker fields. Also T_c decreases with the field, as does the step Q_c in the order parameter. The data at the lowest fields indicate that in zero field the transition may be of second order, and we correlate this with an observed increase of the director fluctuations.

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One of the most studied, and yet poorly understood, types of phase transitions is the nematic-isotropic transition. Since Maier and Saupe [1] published their seminal molecular statistical theory of nematic liquid crystals, more than one hundred experimental and theoretical papers on this transition have been published. Another milestone was the Landau–de Gennes theory [2], which has been used extensively in the analysis of experimental data. Both theories predict a first-order phase transition. Among the most important experimental parameters to measure are the value Q_c of the order parameter Q at the phase transition T_c, and the width $|T_\pm^* - T_c|/T_c$ of the thermal hysteresis. The spinodal points T_+^* and T_-^* mark the stability limit T_+^* of the nematic phase within the isotropic phase, and the stability limit T_-^* of the isotropic phase within the nematic phase. The Maier-Saupe theory gives $|T_\pm^* - T_c|/T_c \sim 0.1$, but recent conceptual and calculational improvements by Tao, Sheng, and Lin [3] and by Zhang, Mouritsen, and Zuckermann [4] have narrowed it down to 0.012 and $\lesssim 0.005$, respectively. There have been no direct measurements of this quantity. Extrapolation of the observed pretransitional behavior of the susceptibility [5] and of the NMR data [6] give, respectively, the values 2.3×10^{-3} and 3×10^{-3}. These data are for the room-temperature liquid crystal 4-methoxybenzylidene-4′-butylaniline (MBBA). We have studied another canonic nematogenic substance, para-azoxy-anisole (PAA), which melts at 119 °C and has a nematic-isotropic transition T_c at 135 °C. There are apparently no experimental data on the width of the thermal hysteresis around T_c. The data on the order parameter Q have been reviewed by Chandrasekhar [7]. At T_c $Q_c = (0.32 \pm 1)$, and Q_c is, like $|T_\pm^* - T_c|/T_c$, a measure of the strength of the first-order character of the transition. The Maier-Saupe theory gives $Q_c = 0.4292$. Recent calculations by Zhang, Mouritsen, and Zuckermann [4] give $Q_c = 0.19$, i.e., a much weaker first-order character. The nature of the transition has been discussed by de Gennes and Prost [8]. In their view the observed temperature dependence of the order parameter may indicate a role of fluctuations in the transition, which even might be of second order.

We have used coherent neutron scattering for studying $Q(T,H)$, the temperature and field dependence of the nematic order parameter, near T_c. Our sample is d-PAA, fully deuterated PAA. It is contained in a parallelepipedic aluminum vessel of inner dimensions $3 \times 3 \times 0.3$ cm^3. One of the long dimensions is vertical and parallel to the magnetic field. The other long dimension is parallei to the horizontal scattering vector. Heating elements at the top and bottom of the vessel, and several thermistors and thermocouples, made it possible to measure and control the temperature to an accuracy of ±0.01 °C. From the temperature variation of the scattered neutron intensity at 1.8 Å^{-1}, the position of the strongest diffraction maximum, the nematic temperature range, on heating, was measured to be from 118.75 to 135.2 °C. The latter value depends on the strength of the applied magnetic field, as shown below.

To a good approximation, the time-averaged intensity at 1.8 Å^{-1} of a field-aligned sample is proportional to Q [9]. For $H < H_c$, i.e., below the threshold (Freedericksz) field for alignment, the thermal fluctuations of the director manifest themselves as temporal fluctuations of the intensity. We have earlier studied these slow fluctuations in real time [10,11] and, by a Hurst-exponent analysis, found a crossover from fractional to ordinary Brownian motion at $H \sim H_c$. At $H \sim H_c$ the amplitude of the slow intensity fluctuations is ~50% of the total, and measuring times of several hours are required for obtaining a reliable average intensity.

Figure 1 shows the time-averaged neutron intensity measured as the temperature was cycled in small steps through the nematic-isotropic transition. The width of the transition is ~0.4 °C at the higher field. It may be intrinsic or due to temperature gradients beyond our control, or both. In any case T_c, as defined from the midpoint F of the hysteresis loop, increases with the field. For the higher field also a thermal hysteresis is clearly resolved. Such an experimental curve could, however, result from measuring times shorter than the orientational diffusion time of the director, or shorter than the time needed for thermal equilibration. That this is not the case is seen

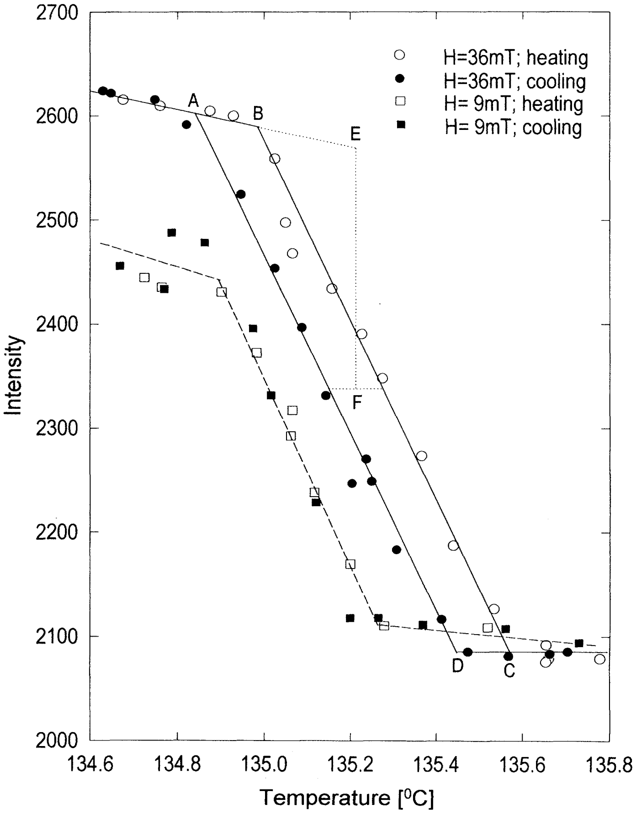

FIG. 1. Thermal hysteresis at the nematic-isotropic phase transition in d-PAA, measured by neutron scattering, and for two values of the applied magnetic field. Lines are guides to the eye.

from Fig. 2. It shows that, after about 5 h waiting time, the subsequent time-averaged intensity will be close to the correct asymptotic value. This curve was measured at increasing temperature, along *BC* of Fig. 1. At decreasing temperature, along *DA*, an asymptotic value was reached in less than 2 h. On the average we used a total of 120 h for each hysteresis loop. Figure 2, which is measured at the middle of the steep part *BC* of Fig. 1, also shows that the temperature control works properly.

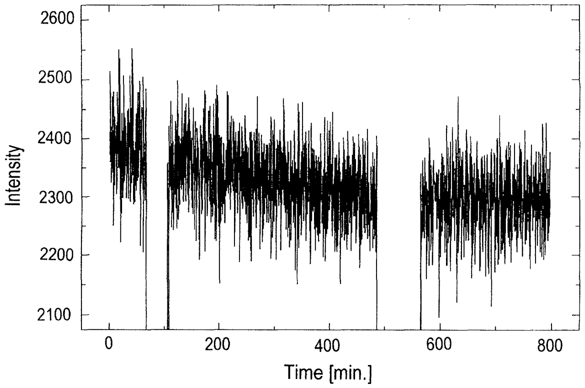

FIG. 2. Slow relaxation of the neutron intensity as the temperature is increased by 0.05 °C. Holes in the intensity record are due to reactor shutdowns.

The threshold field for magnetic alignment is given by [8] $H_c = \pi(K/\chi_a)^{1/2}d^{-1}$, in which d is a characteristic dimension of the sample, K is (in the one-constant approximation) an averaged elastic constant, and χ_a the anisotropic diamagnetic susceptibility. The scattered neutron intensity as a function of the applied field gives a rough measure of H_c. At $T = 119$ °C we have earlier [12] found $H_c \sim 2.5$ mT (25 Oe), in agreement with a calculated value. From theory [8] one expects $K \sim Q^2$ and $\chi_a \sim Q$, i.e., $H_c \sim Q^{1/2}$. Hence we expect H_c to decrease as $T \rightarrow T_c$. This is borne out by the data of Fig. 3, at T_{c-1}, although the large temporal thermal fluctuations of the director, mentioned above, make an accurate measurement of the time-averaged intensity difficult at fields below 10 mT. The effect is particularly strong near T_c, where K gets small.

On the basis of data like those in Fig. 1, and for several other values of the applied magnetic field, we present in Fig. 4 data for the field dependencies of T_c, the step in the order parameter at T_c, and the width $(T_+^* - T_-^*)$ of the hysteresis curve. The step in the order parameter is evaluated from the intensity $I(B)$ at point B (see Fig. 1) and, after subtraction of the background, put on an absolute scale in the following way. The susceptibility data [5] give a value of 0.54 for Q at 119 °C, and we attach

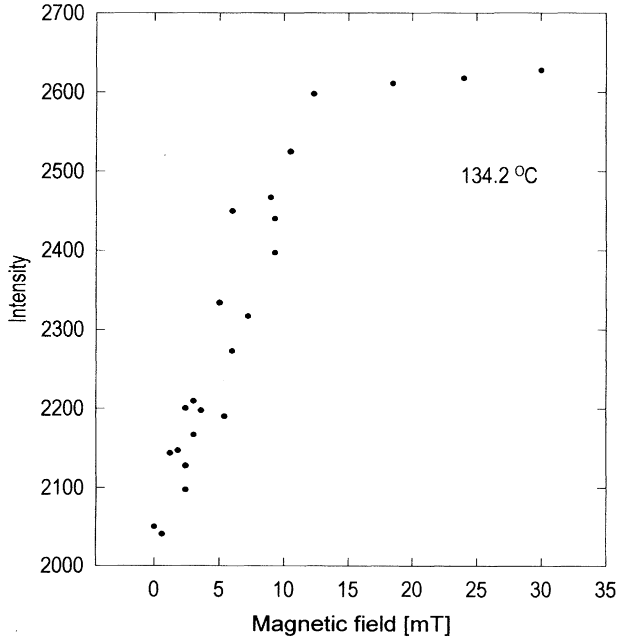

FIG. 3. Neutron intensity as a function of the applied magnetic field, at $T_c - T = 1$ °C. The scattering of points below 10 mT is due to the slow orientational fluctuations of the nematic director.

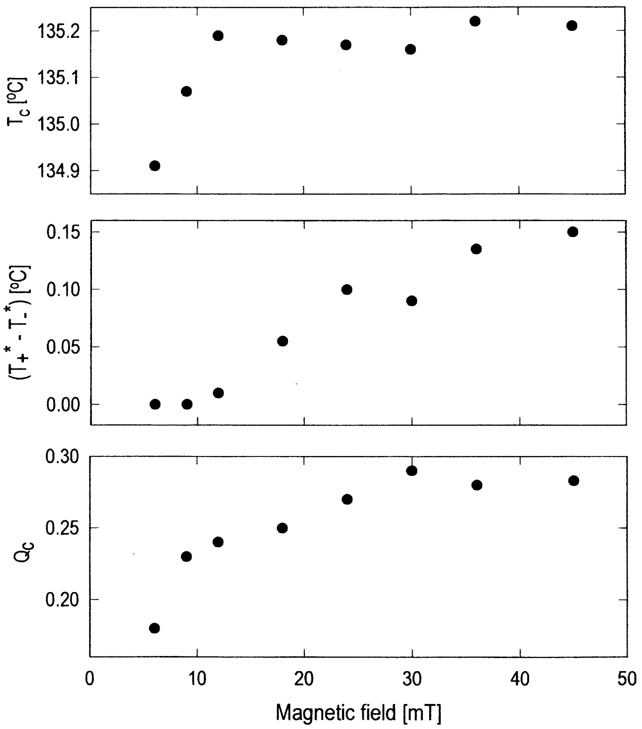

FIG. 4. Magnetic field dependence of the nematic-isotropic transition T_c, the width of the thermal hysteresis $(T_+^* - T_-^*)$, and the step in the order parameter Q_c at T_c.

this value to the neutron intensity $I(119\,°\mathrm{C})$ at the same temperature. Q_c is then calculated from the relation $Q_c = 0.54 I(B)/I(119\,°\mathrm{C})$. The value 0.28 that we arrive at for an aligned sample is lower than the value 0.32 quoted above [7]. Our values for Q_c could thus be systematically ~10% too low, but the downward trend as $H \rightarrow 0$ should be real. We would actually have obtained even lower absolute values of Q_c had we, for its derivation, used the intensity at E (see Fig. 1) instead of at B.

The data of Fig. 4 show that, in the low-field regime, T_c increases with the field. A much weaker field dependence of T_c has been reported earlier by Helfrich [13]. He observed visually a shift of ~0.1 °C for an electric field 3×10^4 V cm^{-1}, which corresponds to a magnetic field of 3 T. Malraison, Poggi, and Guyon [14], however, observed no change of T_c in careful measurements of the enhanced birefringence (IEB) in magnetic fields as high as 15 T. Using Landau theory, they estimated that a field of 10 T would be needed to change T_c by 10^{-2} °C. Neither of these two reports [13,14] were concerned with the behavior in weak fields, $H \sim H_c$, the only regime in which we saw a definite shift of T_c.

The curve in Fig. 3, taken ~1 °C below T_c, has two regimes: a steep part for $H < 12$ mT and a gently, linearly increasing curve for $H > 12$ mT. A crucial question is now whether the steep slope reflects a gradual macroscopic alignment of the molecules only or, in addition, an increase of the order parameter by a reduction of the orientational fluctuations. In Ref. [14] similar high- and low-field regimes were observed in the IEB data, and the authors connected the high-field part only with an increase of the order parameter. In Ref. [11] it was shown that the rather pronounced macroscopic fluctuations of orientation in the low-field part have the same critical behavior as the fluctuations in the magnetization direction in an isotropic three-dimensional Heisenberg ferromagnet. The question raised above can now be rephrased by asking whether, within the continuum theory of nematics, one can clearly distinguish (on the wavelength scale) fluctuations of the director from those of the order parameter. In particular, close to T_c, as the orientational fluctuations soften, such a distinction may not be relevant. Possibly the phase transition may become continuous at $H = 0$, and our data for Q_c and $(T_+^* - T_-^*)$ in Fig. 4 may reflect an incipient behavior for that. In the isotropic Heisenberg model the magnetization M is predicted to behave as $M \sim H^{1/\delta}$ with a critical index $\delta = 5$. Actually our data for Q_c are not inconsistent with such a behavior. It would obviously be desirable to extend the data of Fig. 4 to lower fields, but the concomitant increase of the slow fluctuations renders such experiments very time consuming.

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*On leave from Institute of Physics, Warsaw University Branch, Lipowa 41, 15-424 Bialystok, Poland.

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