High-resolution study of fluctuation effects at the nematic–smectic-*A* phase transition

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1. Introduction and the Experimental Technique

The phase transition from the nematic to the smectic-A phase in thermotropic liquid crystals has been actively studied since the 1970s [1]. In the era of the renormalization group theory, it was perhaps hoped that the nematic–smectic-A (NA) transition would provide a simple model system in which to study a broken continuous symmetry.

Yet, 30 years later fundamental questions remain unanswered. Is the nematic–smectic-A (NA) transition always first order? Experimentally, the transition discontinuities are so weak as to tax the resolution of the finest high-resolution calorimeters. Phase transition order is important to know because for universality to apply at all levels of its hierarchy, the correlation length must diverge continuously to infinity at T_c [2, 3]. Fluctuation effects, well understood in continuous (second order) phase transitions, are yet only partially understood at quantitatively study orientational fluctuations in liquid crystals in real space. Using cross-polarizer optical microscopy, we probe local, temporal fluctuations in light intensity that arise from orientational fluctuations in the nematic phase. In the smectic-A phase, deformations of the nematic director can give rise to layer compression, which is not a soft mode. Thus orientational fluctuations are suppressed in the smectic-A phase. As a result, following optical intensity fluctuations provides a direct way of discriminating between the nematic and the smectic-A phases.

Also vitally important is the temperature control. The temperature control set-up designed and constructed as part of this thesis, provides short-term stability (for the duration of the measurement) of 0.05 mK, and long-term stability of 0.15 mK. In any phase transition measurement, the inevitable existence of spatial temperature gradientcte phase that often occurs in a material composed of rod-like molecules. Although the centre-of-mass of the molecules are disordered, the rods tend to align spontaneously: the nematic phase therefore has orientational order (denoted by a magnitude S and a 'director' n, a headless unit vector giving the local direction of orientational order), but no positional order. The smectic-A phase not only has orientational order like a nematic, it also exhibits a density modulation ('layering') in the direction of the director. It is characterized by a two-component order parameter that captures both the amplitude and the phase of the density modulation.

When an isotropic liquid is cooled into the nematic phase, three-dimensional rotational symmetry is spontaneously broken, and the average direction picked out is usually governed by weaker surface anchoring effects. This has two outcomes. First, one can easily make a single domain nematic (analogous to a single crystal in solid state physics) by controlling the surface treatment of the bounding surfaces. Second, fluctuations of the director are a soft mode in the nematic. Because of this, the nematic has only partial orientational order. In the smectic-A phase orientational fluctuations are suppressed. Thus smectic ordering is intrinsically coupled with an increase in the nematic ordering. This coupling, referred to as the deGennes-McMillan coupling provides a mechanism that can drive the transition first-order when the NA transition is sufficiently close to the isotropic-nematic (IN) transition. Thus an important parameter in the phenomenology of the NA transition is the nematic range, parametrized by the ratio T_{NA}/T_{IN}. In experiments, this effect manifests itself as a linear dependence of the latent heat on mixture concentration in a homologous series of two very similar liquid crystals, with the latent going to zero at a point known as the Landau tricritical point (LTP).

In addition to this coupling, there also exists a more subtle coupling between the smectic order parameter and the nematic director. The anisotropy of the liquid crystal system requires the gradient terms in a smectic free energy expansion to be anisotropic, with the gradient terms parallel and perpendicular to the director having different multiplicative pre-factors. Local fluctuations in the director imply local variations in the gradient direction. Writing this free energy in a covariant form naturally incorporates this coupling. Once again, the strength of this coupling is expected to be large when director fl

derived by them, there was a negative cubic term that would not be allowed in a local free energy. Experimentally, this would imply a non-linear crossover from the linear behaviour of the latent heat as a function of mixture concentration. In the 8CB-10CB system which is close to the small-nematic-range limit, Anisimov et al. [6] showed that there was indeed a non-linear crossover near the Landau tricritical point (LTP) showing that the LTP was not a true tricritical point.

However, the resolution of the adiabatic calorimetry experiments [7] ran out before reaching pure 8CB, where the transition was consistent with being second order. Here, a novel dynamical technique by Cladis and coworkers [8] showed by examining front propagation velocities that even in 8CB the transition was first order. However, while being a good qualitative first test of phase transition order, it did not provide an accurate quantitative estimate of discontinuity strength that could be used to test HLM theory. This experiment highlights the jump in sensitivity that is possible in measuring equilibrium quantities by driving the system slightly out of equilibrium, and provided us with a starting point for our quantitative studies.

3. Results

In our studies, we employed two independent probes of a fluctuation-induced first-order phase transition in the 8CB-10CB system. First we have studied the NA transition in pure 8CB. The fluctuations in the nematic obey a well-defined power law in the nematic phase that extrapolates to zero at a temperature T* (which is like the spinodal point) with an exponent $\xi = 0.5$ (see figure 1). However, before this extrapolated temperature, the fluctuations are discontinuously interrupted by the advent of the smectic-A phase. This discontinuity is characterized by the normalized difference between the transition temperature T_{NA} and the extrapolated temperature T*. Thus we find the transition to be clearly first order, with a dimensionless discontinuity $t_0 = 1.6 \times 10^{-5}$.

We then explored theoretically [9] the effect of an external applied magnetic field on the phase transition. The prediction from this theoretical analysis, which is essentially an extension of the HLM theory, was a linear suppression of the zero-field discontinuity. Moreover, we predicted a field-induced tricritical point at a modest value of the magnetic field. In 8CB, this tricritical point was estimated to be about 10 T. This implied an easily

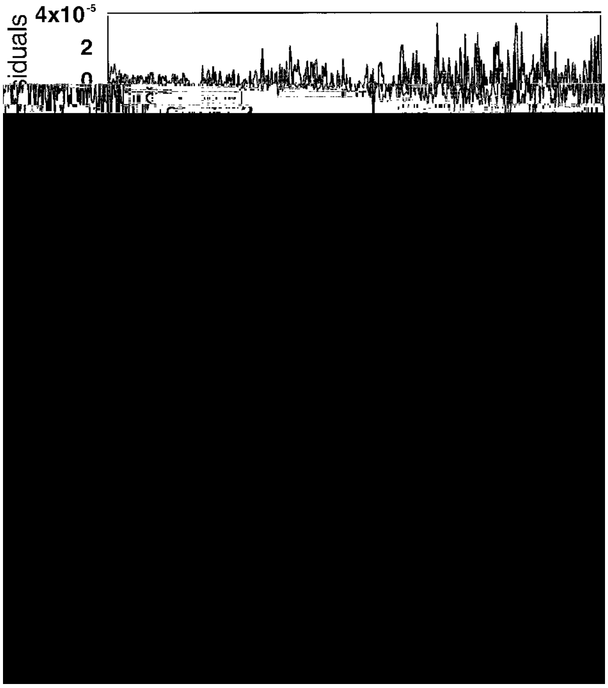

Figure 1. Pure 8CB, $d = 30\,\mu m$, 0.59 ± 0.02 K/cm. Here $t_0 = (5.0 \pm 0.5$ mK$)/(307$ K$) = 1.6 \pm 0.1 \times 10^{-5}$. Results are shown with and without an external applied magnetic field.

unambiguously measure a depression as small as 10%. This sets a lower bound on the critical field, in all the experiments, of 30 T.

We do, however, measure the expected non-critical magnetic field effect, the suppression of the fluctuations in the nematic phase. The suppression of the variance goes as H^2, as expected. ffi

. This, in turn, is internally consistent with our

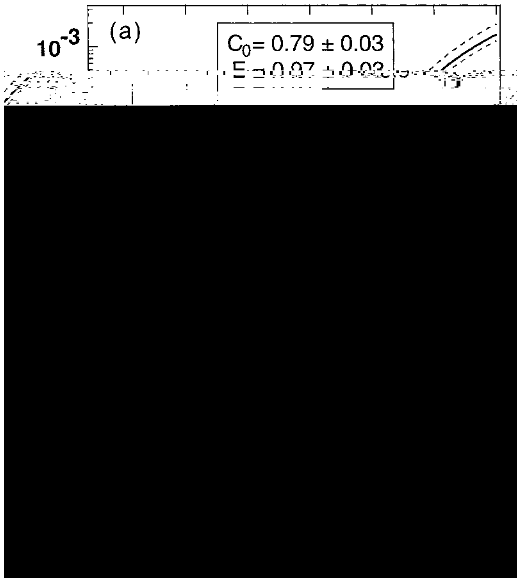

Figure 2. (a) Fit of t_0 data to the Anisimov parameters ([6]) with C_0 and E as fit parameters. Top and bottom dashed curves show fits for $\xi = 0.6$ and $\xi = 0.4$, respectively ($n = 0.5$ is the fitted exponent to the power law observed). (b) Comparison of latent heat data ([7]) to t_0 data (this work). Open circles: data taken from [7]; filled circles: t_0 data converted to equivalent latent heat.

the negative cubic term in the effective smectic free energy, which is induced by director fluctuations, should get smaller with increasing nematic range.

4. Conclusions

These experimental results [10, 11] are robust and suggest an unambiguous deviation from both the deGennes-McMillan form and HLM theory. Our new

better, in a range that is outside that of adiabatic calorimetry. We presented thre

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(which is mean field in the smectic order parameter) close to the LTP, as originally observed in our experimental work. This is promising, as it is the first quantitative comparison between experiment and theory in the region beyond the LTP where smectic fluctuations begin to be important. Because the question of phase transition order has wide ramifications in the understanding of measured critical exponents, the search for the tricritical point at the NA transition remains interesting.

Additional note. Recently, I. Lelidis [13] measured the effect of an external electric field along the nematic director and concluded that the NA transition in 8CB becomes second order at a field of 13V/μm. This is roughly equivalent to an external field of 130 T, which is consistent with our results.

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