Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Using Nematic Director Fluctuations as a Sensitive Probe of the Nematic-Smectic-a Phase Transition in Liquid Crystals

Anand Yethiraj [a] & John Bechhoefer [a]

[a] Dept. of Physics, Simon Fraser University, Burnaby, British Columbia, V5A 1S6, Canada

Version of record first published: 04 Oct 2006

To cite this article: Anand Yethiraj & John Bechhoefer (1997): Using Nematic Director Fluctuations as a Sensitive Probe of the Nematic-Smectic-a Phase Transition in Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 304:1, 301-307

To link to this article: http://dx.doi.org/10.1080/10587259708046974

Mol. Cryst. Liq. Cryst., 1997, Vol. 304, pp. 301–307
Reprints available directly from the publisher
Photocopying permitted by license only

USING NEMATIC DIRECTOR FLUCTUATIONS AS A SENSITIVE PROBE OF THE NEMATIC–SMECTIC-A PHASE TRANSITION IN LIQUID CRYSTALS.

ANAND YETHIRAJ AND JOHN BECHHOEFER
Dept. of Physics, Simon Fraser University, Burnaby, British Columbia, V5A 1S6, Canada

Abstract We present a new, extremely sensitive optical method to study the nematic–smectic-A (NA) phase transition in liquid crystals. In this new technique, we monitor nematic director fluctuations as a function of temperature as we approach the NA transition. We show that the NA transition in the liquid crystal 8CB (which has a small nematic range) is clearly first order, well within the resolution of the experiment. This is contrary to previous calorimetric measurements but confirms an earlier dynamical measurement. We characterize the strength of the phase transition by a dimensionless, technique-independent quantity $t_0 = (T_{NA} - T^*)/T_{NA}$. For 8CB, we measure $t_0 = (6 \pm 2) \times 10^{-6}$.

INTRODUCTION

The nature of the nematic–smectic-A (NA) phase transition in liquid crystals has long been a contentious, unsolved problem in condensed-matter physics.[1–4] In the nematic phase, molecules align along a common direction $\hat{n}$ (the "director") but have no positional order. In the smectic-A phase, in addition to orientational order, there is also a density modulation in the direction of the average director, which can be identified with layering normal to the director. One might then expect the NA transition to be a relatively simple one-dimensional crystallization. However, both experimentally and theoretically, the study of this transition has proved to be much more complicated and interesting.

An as-yet-unresolved point concerns the order of the transition. Mean-field theory predicts a second-order transition for liquid crystals with a large nematic range ($T_{NA}/T_{NI} \ll 1$) and a first-order transition for liquid crystals with a small nematic range ($T_{NA}/T_{NI} \to 1$)[1]. The crossover (known as the tricriti-

cal point) is predicted to be at $T_{NA}/T_{NI} = 0.87$. When the nematic range is small, the large order-parameter fluctuations near the NI transition can couple to the emerging smectic order parameter ψ at the NA transition, providing a mechanism for a fluctuation-induced first-order phase transition[5]. For an "infinite" nematic range ($T_{NA}/T_{NI} \to 0$), the transition is predicted to be second order and in the same universality class as the (inverted) 3D XY model. Numerical simulations[6] predict a tricritical point for strong-enough nematic fluctuations, but it is not clear whether actual materials ever have a large enough range to have a "true"[7] second-order phase transition. (The largest known nematic range is $T_{NA}/T_{NI} = 0.67$.) Experimentally, high-resolution calorimetric techniques[8,3] have found the transition to be indistinguishable from second-order for liquid-crystals with $T_{NA}/T_{NI} < 0.98$. These results are not conclusive, however, because a dynamical measurement by Cladis *et.al.*[9] implied that 8CB (a cyanobiphenyl liquid crystal with $T_{NA}/T_{NI} = 0.977$) in fact has a first-order NA transition.

THE EXPERIMENT

In this work, we present a new and extremely sensitive experimental method for probing the NA transition. There are three kinds of elastic distortions in the nematic phase :splay, bend and twist. All three deformations contribute to orientational fluctuations. In the smectic phase, however, twist and bend would compress the layers, which costs much energy. Hence, only splay distortions are allowed, and the magnitude of the fluctuations in the smectic is appreciably smaller. In our method, we track the director fluctuations as a function of temperature directly in real space, via crossed-polarizer optical microscopy. Since nematic and smectic materials are birefringent, when a uniaxial planar-anchored liquid crystal is placed at an angle θ with respect to the polarizer, the light exiting the analyzer has an average intensity $I \propto \sin^2(2\theta)$. In other words, to a first approximation, the liquid crystal acts like a waveplate. Local fluctuations in the director result in local intensity fluctuations. Using cross-polarized optical microscopy, we can image a large area of the liquid crystal (1 mm^2), which is equivalent to an ensemble of domains with different orientations.

The image is captured on a computer via a Pulnix TM7 8-bit CCD camera and a Scion LG3 framegrabber card. Each pixel on the CCD camera, which corresponds to just under a 2μm$\times 2\mu$m area of the sample, spatially averages small-scale fluctuations. (An upper limit on the spatial scales probed is set by the sample thickness, which typically is on the order of tens of μm.) The camera's electronic shutter is set at 1/250 sec., which is the scale of the fastest fluctuations resolved by our microscope system. We capture 32 images at 0.2 second intervals. From this time-series, we calculate an average intensity (I) and a root-

mean-squared difference (F) for each pixel in the image. The latter quantity F is a measure of the strength of the fluctuations. Normalizing F by I makes it independent of the light intensity, and thus independent of variations in illumination across the sample. Because of the large number (300,000) of pixels in each image, we obtain an intensity resolution of 1/100th of a gray level. A subtlety is that the fluctuation signal is caused not only by director fluctuations but also by various types of noise; however, because the light intensity is high, the dominant contribution comes from photon shot-noise. Note that the contribution due to orientational fluctuations $\propto I$, whereas shot noise is $\propto I^{1/2}$. Since the director fluctuations and shot-noise are independent, the noise is subtracted in quadratures from F. The value of F in the nematic phase is well above the noise level, while in the smectic-A phase it is above the noise-level by a mere 1/50th of a gray level. (See Fig. 1.) However, even the smectic signal can be resolved from the background.

The liquid-crystal cells are sandwiched between two glass plates that are separated by spacers to control the thickness (typivally set to 15 μm). Because the fluctuation signal depends on sample thickness, we take care to have a uniform sample thickness. By observing interference fringes while the glue sets we have variations of less than 0.1 μm over the 1 mm field of view. The glasses are treated

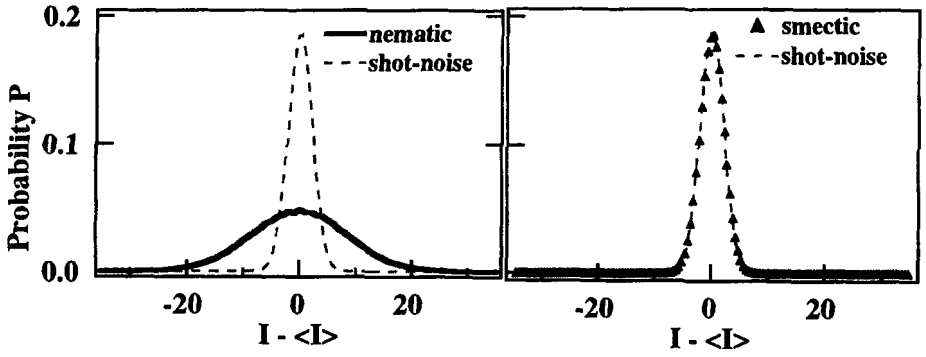

FIGURE 1 Histogram of intensity fluctuations in (a) the nematic and (b) the smectic phase. The photon shot-noise at the same intensities is presented for comparison. In (b), the difference between the smectic and shot-noise distributions, although not discernible to the eye, is statistically significant.

for planar, unidirectional anchoring of the liquid crystal. The sample so made is placed in a commercial temperature-controlled oven whose long-time stability is approximately 0.01 K. To increase the time-constant of oven-temperature fluctu-

ations, we enclose the sample in a copper cell. The sample temperature then is stable to a fraction of a mK over the few seconds it takes to acquire the images.

RESULTS AND DISCUSSION

Armed with our new technique, we have probed the order of the transition for 8CB. For temperatures well above T_{NA}, we simply measure $F(T)$. Very close to the transition, residual temperature gradients inside the cell result in part of the sample being nematic and part smectic-A, with a locally flat boundary separating the two phases. Since the fluctuations so close to the transition are decreasing very rapidly with temperature, assuming every pixel in the image to be identical results in an unforgiving smearing of the data. Instead, turning this problem to our advantage, we devised the following trick to improve our resolution: we divide our image into strips parallel to the NA boundary, which in practice is straight, on the length-scale of an image. Each strip then corresponds to a slightly different temperature. Measuring F for each strip as a function of its distance from the NA boundary is equivalent to measuring F as a function of temperature.[10]. To calibrate position against temperature, we made very small changes in the oven-

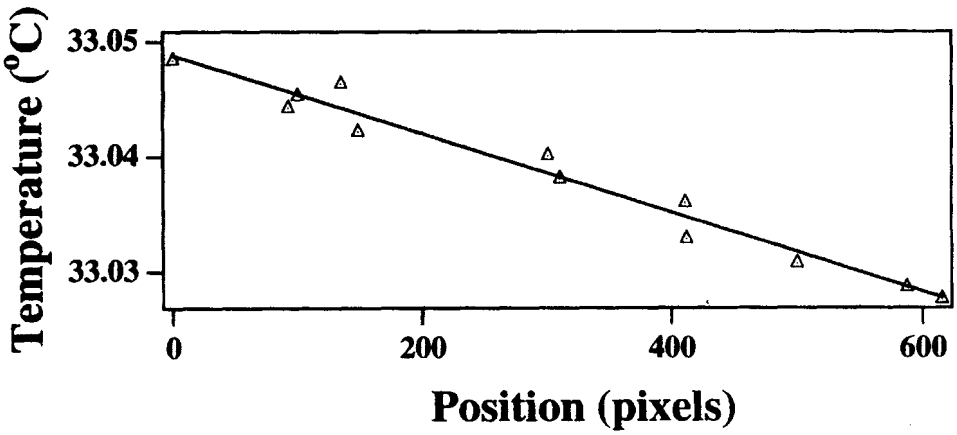

FIGURE 2 Calibration of interface position *vs.*temperature. The lateral gradient is given by the slope G = $(3.2 \pm 0.2) \times 10^{-5}$ K/pixel.

temperature near the NA transition and observed that the NA boundary moved to new positions within the field of view. Each image that contains an NA inter-

face is "self-calibrating" in that over small times, the gradient remains constant while the overall temperature fluctuates slowly. Different images are then merely translated with respect to each other and are easily aligned. Making several such temperature changes, we obtained a linear graph of boundary position *vs.* temperature (Fig. 2). The slope of this graph is $(3.2 \pm 0.2) \times 10^{-5}$ K/pixel. In practice, a relatively large vertical gradient smears out the data, but we still have a temperature resolution of a fraction of a milliKelvin. The resulting graph of F *vs.* T is shown in Fig. 3(a). The nematic side can be fit to a power law; the smectic side can be fit to a flat line. At the boundary, there is a linear interpolation between nematic and smectic regions, which results from the smearing due to the vertical temperature gradient. The important point is that there is an abrupt change at the NA transition. The fit was done over the largest temperature range that still kept the residuals (plotted in Fig. 3(b)) flat. The fitted power-law extrapolates to a temperature below that of the interface. This has a simple, self-consistent interpretation: close to the NA transition, smectic fluctuation domains in the nematic phase suppress the nematic fluctuations. The coupling between nematic and smectic order parameters is weak enough not to play a role until very close to T^*, when it cuts off the power-law variation of F and causes a discontinuity. The temperature T^* is a phantom divergence point, and the extent of the metastable region $(T_{NA} - T^*)$ is a measure of the strength of the first-order phase-transition. We extract the quantity $t_0 = (T_{NA} - T^*)/T_{NA}$ from the graph. This quantity is a dimensionless measure of the strength of this first-order phase transition and has a numerical value of $(6 \pm 2) \times 10^{-6}$., which corresponds to $(T_{NA} - T^*) = (2.0 \pm 0.5)$ mK . Most of the uncertainty comes from the smearing due to the vertical gradient. (By contrast, the NI transition in 8CB has $t_0 \simeq 3 \times 10^{-3}$, and a typical solid-liquid transition probably has $t_0 \simeq 1$, although it is not clear whether the liquid phase ever becomes unstable.) An advantage of using t_0 as a measure of the discontinuity of the transition is that it lets us compare results from different measurement techniques (calorimetry, scattering, etc.) For example, the measurement of Cladis *et.al.*[9] implies, according to our estimates, a t_0 in a range between 2×10^{-6} and 2×10^{-5}.

CONCLUSIONS

In conclusion, we have created a new experimental probe of the NA transition. In contrast with light scattering, where longer wavelengths are progressively harder to probe, they are progressively easier in microscopy. Another significant advantage of microscopy is that we can use the temperature gradient within the cell to improve the temperature resolution quite dramatically. Although the resolution we have of the fluctuation signal and the temperature is already good, we have

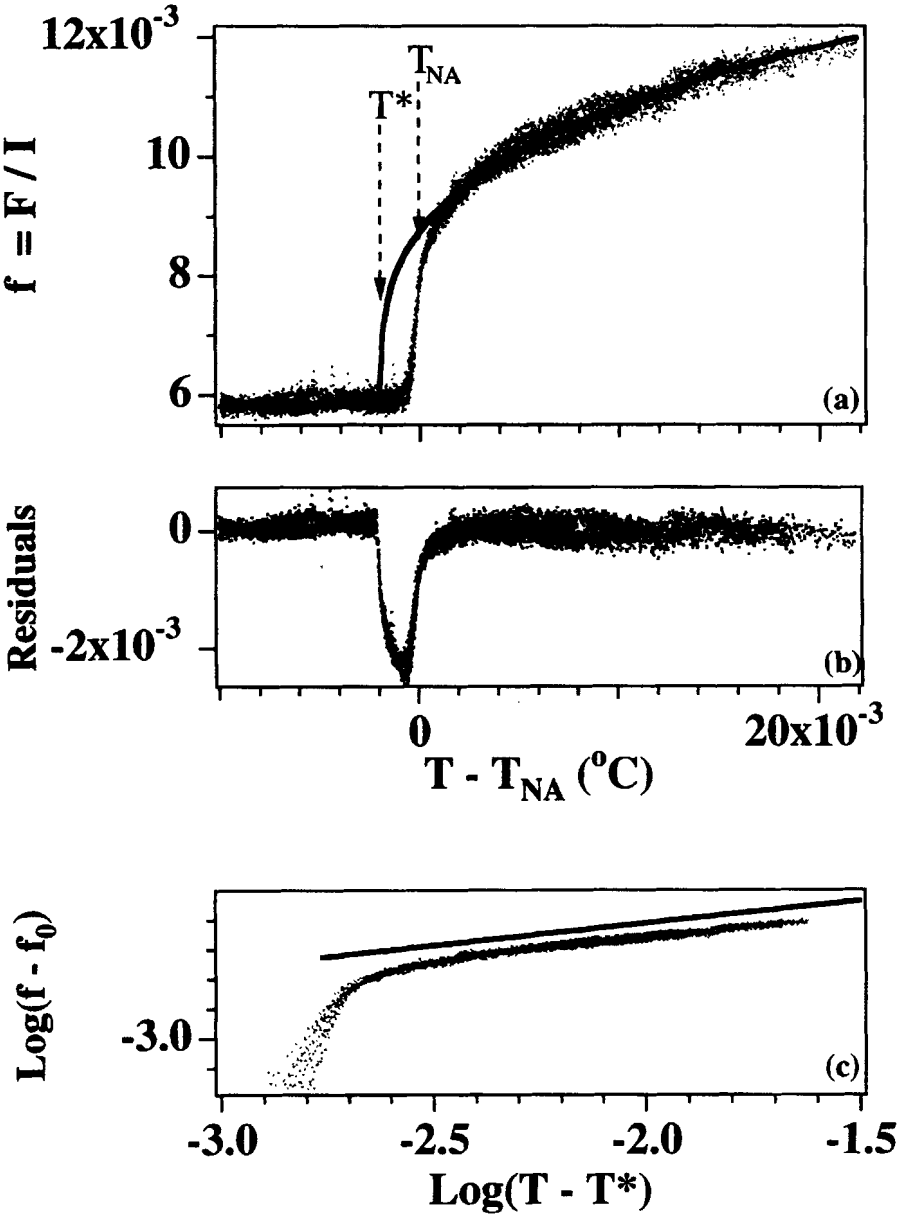

FIGURE 3 Normalized fluctuation-temperature (f *vs.* T) curve for a 7.5 μm thick sample of 8CB. (a) The data and the best-fit power-law $f = f_0 + f_1(T - T^*)^y$ (b) The residuals: fit is carried out over the largest region over which the residuals are flat (c) log-log plot: best-fit line has a slope of 0.30 ± 0.05, consistent with 3D XY predictions, but not ruling out other possibilities.

yet to reach any fundamental limits, and we hope to improve each by atleast an order of magnitude with better temperature-control (for overall stability and especially for gradients) and a better CCD camera. With these improvements, we plan to search for the proposed NA tricritical point. We have found the NA transition in the liquid crystal 8CB to be first order with a dimensionless strength $t_0 = (6 \pm 2) \times 10^{-6}$. We would like to acknowledge useful discussions and on-going theoretical work by Michael Plischke and Paul Lammert. This work was supported by a research grant from NSERC (Canada).

REFERENCES

1. *The Physics of Liquid Crystals*, P. G. de Gennes and J. Prost, (Oxford Univ. Press), 1993.
2. C. W. Garland and G. Nounesis, Phys. Rev. E 49, 2964 (1994).
3. W. G. Bouwman and W. H. de Jeu, in *Modern Topics in Liquid Crystals*, edited by A. Buka (World Scientific, London, 1993).
4. M. A. Anisimov, Mol. Cryst. Liq. Cryst. 162A, 1 (1988)
5. B. Halperin, T. C. Lubensky, S. K. Ma, Phys. Rev. Lett. 32, 292 (1974).
6. C. Dasgupta, Phys. Rev. Lett. 55, 1771 (1985); J. Phys. Paris 48, 957 (1987).
7. Experimentally, one can rule out a second-order transition by, for example, measuring a non-zero latent heat, but one cannot rule out a first-order transition so weak that it has a latent heat smaller than the experimental resolution.
8. H. Marynissen, J. Thoen, and W. van Dael, Mol. Cryst. Liq. Cryst. 97, 149 (1983); J. Thoen, H. Marynissen, and W. van Dael, Phys. Rev. Lett. 52, 204 (1984).
9. P. E. Cladis, W. van Sarloos, A. Huse, J. S. Patel, J. W. Goodby, and P. L. Finn, Phys. Rev. Lett. 62, 1764, (1989); M. A. Anisimov, P. E. Cladis, E. E. Gorodetskii, D. A. Huse, V. E. Podneks, V. G. Taratuta, W. van Sarloos, and V. P. Voronov, Phys. Rev. A 41, 6749 (1990).
10. Very close to the tricritical point, this "adiabatic" approximation will break down. We will consider this point in a future publication.