CHAPTER 8

RECENT EXPERIMENTAL DEVELOPMENTS AT THE NEMATIC TO SMECTIC-A LIQUID CRYSTAL PHASE TRANSITION

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1. INTRODUCTION

Continuous phase transitions are characterized by universality: thermodynamic observables that diverge with power-law exponents whose values are governed by symmetry considerations and are insensitive to other details of the materials [1, 2]. The nematic-smectic-A (NA) transition, where an ordered liquid acquires additional one-dimensional periodicity is one of the outstanding unsolved problems in this field of study [3, 4]. Here the critical behaviour appears non-universal. The order of the transition has been a matter of debate. The complexity of the NA transition arises from an intrinsic coupling between two order parameters. Indeed, even the direct determination of mean-field parameters has been a matter of recent study. Due to this complexity, there are still unresolved issues after more than three decades of research. The subtleties involved have been addressed theoretically via different approximations, leading to a rich addition to the phase transitions literature. Experimentally, these subtleties have inspired precise high-resolution experiments. This article focuses on experimental developments in the last decade that address aspects of the nature of the NA transition.

2. BACKGROUND: THE HIERARCHY OF THEORETICAL APPROXIMATIONS

2.1 Essential Features of the NA Transition

On cooling from the isotropic to the nematic phase, three-dimensional rotational symmetry is spontaneously broken. The average direction of orientation is termed the director. A smectic-A phase has, in addition, one-dimensional positional order

A. Ramamoorthy (ed.), Thermotropic Liquid Crystals, 235–248.

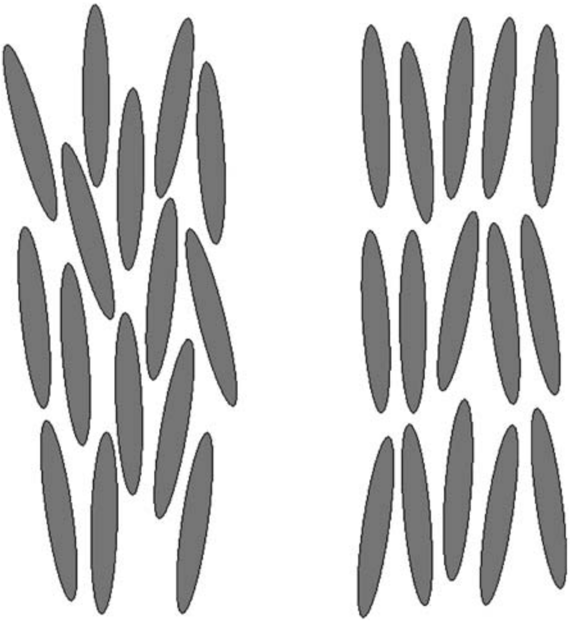

Figure 8-1. A cartoon of the nematic (left) and the smectic-A (right) phase. The nematic phase has only orientational order and no translational periodicity. The smectic-A phase exhibits, in addition, a sinusoidal density modulation (“layering”) in the direction of the orientational ordering; this layering suppresses, but does not remove, orientational fluctuations

in the form of layering, with the layer normals being along the director (see cartoon in Figure 8-1). Since the layer normals must lie along the director, the onset of smectic layering has the effect of suppressing fluctuations of the nematic director (see Ref. [3], Chapter 10 for a good introduction).

This intrinsic coupling between nematic and smectic-A order parameters is crucial to the understanding of the NA transition. The nematic order parameter is a symmetric, traceless second-rank tensor, $Q_{ij} = S\left(3\hat{n}_i\hat{n}_j - \delta_{ij}\right)/2$, where S describes the degree of nematic ordering and $\hat{n}$ gives the direction of that ordering.

The smectic phase is envisaged as a one-dimensional density wave of the form

$$\rho(z) = \rho(0)\left[1 + \frac{1}{\sqrt{2}}|\psi(z)|\cos(q_0 z - \phi)\right] \tag{8-1}$$

where $\frac{2\pi}{q_0}$ is the smectic layer spacing. One can express the smectic order parameter as a complex number $\psi(z) = |\psi(z)|\exp(i\phi)$ whose magnitude is proportional to the amplitude of density modulations in the layered smectic phase and whose phase gives the origin in a given coordinate system.

In the nematic phase, one can induce macroscopic orientation by controlling the surface boundary conditions. However, because nematic ordering is the result of a spontaneously broken symmetry, fluctuations of the director $\hat{n}$ are a soft mode. Indeed a macroscopically oriented nematic phase is much more turbid than a macroscopically oriented smectic-A phase because of light scattering from orientational fluctuation domains. The layered structure of the smectic-A phase suppresses these orientational fluctuations, and it is this coupling that affects the character of the transition (see [5] for a broad survey of such phase transitions). However, smectic phases exhibit one-dimensional orientational order, characterized by the Landau-Peierls fluctuation of the layer spacing [6, 7]. As a result, the essential features needed to capture the NA transition are:

1. Fluctuations of the nematic order parameter S.
2. Fluctuations of the nematic director $\hat{n}$.
3. Phase fluctuations of the complex smectic order parameter ψ.

2.2 Mean-field Theory and Landau–de Gennes Theory

There are several levels of approximation possible in the consideration of the NA transition. First there is the self-consistent mean field formulation due to Kobayashi and McMillan [8–10]. This is an extension to the smectic-A phase of the self-consistent mean-field formulation for nematics ("Maier-Saupe theory" [11]). Kobayashi-McMillan (K-M) theory takes into account the coupling between the nematic order parameter magnitude S with a mean-field smectic order parameter. In Maier-Saupe theory, the key feature of the nematic phase - the spontaneously broken orientational symmetry - is put in by hand by making the pair potential anisotropic. In the same spirit, the K-M formulation puts in by hand a sinusoidal density modulation as well as the nematic-smectic coupling.

In the mean-field picture one expects the phase transition to be generically second order. However, as one adjust materials parameters to reduce the temperature width of the nematic phase, parametrized in K-M theory by the dimensionless ratio T_{NA}/T_{IN}, the coupling drives the transition first order, with the point in material-parameter space where this happens being termed the "Landau Tricritical Point" (LTP).

The Landau-deGennes theory is based on the formal analogy between smectics and superconductors [12, 3]. Within the context of this analogy, there are type-1 and type-2 smectics. As will be seen in the next section, there are well-defined, testable predictions in the extreme type-1 limit. On the other hand, there is also agreement between experiment and the results from a Monte-Carlo simulation by Dasgupta [13] in the extreme type-2 limit. However, the superconducting analogy is imperfect, and in real smectics there appears to be a broad experimental "crossover" region in between these two limits. Varying T_{NA}/T_{IN} (by choosing a variety of liquid crystal preparations with varying nematic range) takes the transition from the small-nematic-range type-1 limit (where the transition is also first order) to the large-nematic-range type-2 limit, where the transition is continuous.

2.3 Thermal Fluctuations

Thermal fluctuations modify critical exponents from the values predicted by mean-field theory [2]. Based on the dimensionality (d = 3) and the order parameter symmetry (n = 2), the NA transition should belong to the isotropic 3DXY (n = 2, d = 3) universality class.

Thermal fluctuations have another effect that is less understood [5]: when two order parameters are simultaneously present and interact with each other, the fluctuations of the additional order parameter may profoundly alter the phase transition of the underlying system. In high-energy physics, for example, such a situation occurs in the Higgs mechanism [2, 14], where the fluctuations of a scalar field can add mass to the soft modes of the underlying transition. In condensed-matter physics, Halperin, Lubensky, and Ma (HLM) [15] predicted 3 decades ago that fluctuations of an additional order parameter could force a system with a second-order phase transition to be first order. The HLM mechanism takes into account the coupling between ψ and the nematic director fluctuations $\delta\vec{n}$. An effective free energy dependent only on ψ is calculated by integrating out the nematic director fluctuations. The theory treats the nematic fluctuations in the Gaussian approximation but is mean field in ψ. They noted two settings where this should occur: the normal-superconducting phase transition in type-1 superconductors and the nematic–smectic-A (NA) transition in liquid crystals [12]. While experiments in superconductors are well-described by mean-field theory, the importance of fluctuations in soft condensed matter makes the effect observable at the NA transition when material parameters have been chosen so as to be in the "type-1" limit.

Order parameters that exhibit large-distance correlations can be influenced strongly by external fields. A recent theoretical extension of the HLM study considered a liquid crystal in the presence of an external field [16] and found that the term in the free energy that is responsible for the HLM first-order character can be suppressed at relatively moderate fields; i.e. 10 T for a magnetic field and 1 V/μm for an electric field. The testing of these predictions is an important recent experimental development, discussed in the next section. It has also been shown [17] that allowing for ψ fluctuations in a type-I superconductor or a liquid crystal always increases the size of the first-order transition. So the HLM prediction that the NA transition is always first order is on firm theoretical ground in the type-1 limit.

With one-dimensional periodicity, the smectic phase cannot exhibit true long-range order due to the Landau-Peierls instability [6, 7]. An anisotropic scaling analysis [18] (see [3], page 521 for a summary) predicts the divergence of the layer compression modulus $B \propto \xi_{\|}/\xi_{\perp}{}^{2}$, thus a divergence with exponent $\phi = \nu_{\|} - 2\nu_{\perp}$. In addition anisotropic scaling allows for three possibilities for the fixed point of the nematic splay elastic constant: $K_1{}^* = 0$, implying $\mathsf{A}_\nu \equiv \nu_{\|}/\nu_{\perp} = 1$, $K_1{}^*$ finite, implying $\mathsf{A}_\nu = 2$, and $K_1{}^*$ infinite, implying $\mathsf{A}_\nu > 2$. The Nelson-Toner anisotropic analysis [19] predicts $\mathsf{A}_\nu = 2$. All options imply either a strong anisotropy ($\mathsf{A}_\nu \equiv \nu_{\|}/\nu_{\perp} \geq 2$ or no anisotropy at all $\mathsf{A}_\nu \equiv \nu_{\|}/\nu_{\perp} = 1$. Experimentally, a *weak anisotropy* $1.08 < \mathsf{A}_\nu < 1.6$ is observed, in contradiction with all the above possisibilities!

The main difficulty with the analogy to superconductors is that the the additional length associated with the nematic splay elastic constant K_1 breaks gauge symmetry. Thus the splay elastic constant does not diverge at the transition. Results based on the superconducting(SC) analogy need to be transformed back into the liquid crystal (LC) gauge in order to be valid. Even isotropic exponents in the SC gauge could become anisotropic after the transformation [20] to the LC gauge. Patton and Andereck [21, 22] analyzed a model based on the Landau-deGennes free energy functional without invoking the analogy to superconductors. They found that the correlation length exponents parallel and perpendicular to the nematic director have different renormalizations, resulting in different values for the exponents $\nu_{\parallel}$ and $\nu_{\perp}$. They found too a curious temperature-dependent crossover from weak to strong anisotropy as one came closer the the transition. While weakly anisotropic critical exponents are clearly the norm in experiments at the NA transition, and this is the only theory to predict them, no quantitative test of Patton-Andereck theory has been achieved. The theory also makes no statements about phase transition order.

Another field-driven fluctuation effect recently predicted is that the fluctuation-induced Casimir-like force between two surfaces bounding a smectic film - one a solid surface and the other a nematic–smectic interface - can be driven from repulsive to attractive in the presence of an external field [23]. Experimentally this should manifest itself by a transition from complete to incomplete wetting at the nematic–smectic interface on increasing an electric field from zero to 10 kV/mm. The presence of this effect has not yet been probed experimentally.

3. EXPERIMENTS PROBING MEAN FIELD PARAMETERS

Experimental developments in the field of liquid crystals are well discussed in a recent collection of reviews [24]. In what follows various recent experimental developments at the NA transition are presented in a form that follows the hierarchy of theoretical approximations within which they were analyzed, beginning with mean-field behaviour.

Realistically, the mean-field K-M formulation is only complete when coupled with experimentally measured values for the model parameters. NMR spectroscopy probes local molecular order. Thus data from NMR spectra are well suited for quantitative fitting to molecular models [25, 26].

3.1 Dissolved Solutes

Molecular order in liquid crystals has been studied extensively by NMR spectroscopy [25, 26] using dissolved solutes as probes of the local environment. Investigations into this problem have used rigid and flexible solutes as probes of the anisotropic environment [26–28] as well as liquid crystal molecules themselves [25]. The dipolar interaction, which averages to zero when the solutes are free to tumble in an isotropic solvent, is non-zero in a liquid-crystalline (anisotropic) solvent giving rise to complex spectra even for simple molecules [29]. These dipolar coupling induced splittings present a wealth of information from which one may calculate the order matrix [26, 30].

The concentration of dissolved solute in NMR studies is typically 1 mole % or larger. Such concentrations can have an effect on more subtle effects such as phase transition order in weakly first-order phase transitions. However, it is an excellent probe of mean-field effects, especially when the effects are probed for different solutes and the results found solute independent. Orientational order in some smectic-A phases changes less rapidly as a function of temperature than in the nematic phase with no break at the phase transition [31–34].

Molecular order in the smectic-A phase was probed recently via a proton NMR study of three aromatic solutes in the liquid crystal 8CB [35]. The results were analyzed in the context of a simple modification of K-M theory for dissolved non-uniaxial solutes. The smectic solute Hamiltonian was written in the form:

$$(8\text{-}2) \qquad H_A = -\tau' \cos(2\pi Z/d) + H_N(1 + \kappa' \cos(2\pi Z/d))$$

where κ' and τ' are the nematic-smectic-A coupling and the smectic order parameter magnitude - fit parameters in the experiment. This tested the applicability of a mean-field Hamiltonian that accounted for both nematic and smectic-A ordering and fully determine the Hamiltonian prefactors κ' and τ'. While τ' was temperature-dependent and solute-dependent, the nematic–smectic-A coupling was found to be a solute-independent liquid-crystal quantity: $\kappa' \approx 0.9$. While measurements of the smectic order parameter have been made since McMillan [10] this is the first measurement of the coupling term found by the author.

Recent optical experiments have probed the effect of flexible polymeric solutes in both lyotropic [36] and thermotropic liquid-crystal [37, 38] environments. Long-chain solutes feel an average effective anisotropy, and are found to exhibit much stronger ordering than smaller solutes. The synthesis of the bent-core mesogens ("banana" molecules) has resulted in a novel biaxial smectic-A (both pure phase [39] and solute-induced [40]) as well as nematic phases [41, 42].

An intriguing experiment with a long flexible polymer dissolved in the liquid crystal 8CB [43] has found that while the polymer predominantly aligns along the primary orientation direction (perpendicular to the smectic layers or along the layer normal), a sizeable fraction ($\approx$ 10%) lies in the direction perpendicular to the layer normal. While this would not be surprising if one pictured the smectic structure as a "bookshelf" geometry, the surprise arises because it has been well established that the smectic density is a square-wave but a sinusoidal modulation [44]. The field of solutes in thermotropics is thus seeing a resurgence.

3.2 Carbon-13 and Deuterium NMR Studies

The cleanest way to eliminate the effects of a solute is to have no solute. Recently a method which uses carbon-13 NMR [45] and one that uses deuterium NMR [46] to study the reorientation of a smectic liquid crystal has been reported. Both studies concentrate on macrodomain reorientation in a single phase. The carbon-13 NMR method, which turns off and on near-magic-angle spinning in order to achieve reorientation, can be used in both nematic and smectic-A phases, and can thus be used as a way to probe the NA transition.

The NA transition in a series of homologous liquid-crystalline compounds, nO.m (4-n-alkoxybenzilidene-4'-n-alkylanilines), has also been probed by carbon-13 NMR [47]. The order parameters were determined by a two dimensional technique called separated local field spectroscopy combined with off-magic angle spinning. NMR probes local order parameters of different molecular segments, and so the behaviour of different molecular segments can be followed simultaneously. Changes in the order parameters of the different molecular segments were quantitatively related to the McMillan ratio, and the Landau Tricritical Point in this series of mixtures was located by this technique.

4. EXPERIMENTS PROBING CRITICAL BEHAVIOUR

A comprehensive review of the study of critical phenomena at the NA transition is not attempted here. The reader is pointed to excellent reviews of this literature (see e.g. Ref. [48] and Ref. [49] and references therein). High-resolution calorimetry results produced a consensus that the NA transition in most liquid crystals is second order. The main issue that remained was to rationalize the large spread in critical exponents observed on different liquid crystals with varying nematic range (characterized by the McMillan ratio T_{NA}/T_{IN}, which is a material-dependent number), with the critical exponents approaching 3DXY values for large nematic range. At smaller nematic range, it appeared (see [48]) that there was a broad crossover in critical exponents from 3DXY to tricritical. The critical exponent anisotropy $\mathrm{A}_\nu \equiv \nu_\parallel/\nu_\perp \approx 1.08 - 1.6$ depending on T_{NA}/T_{IN} (Figure 8-2).

This was qualitatively consistent with predictions by Patton and Andereck. But the main prediction of Patton-Andereck theory was that the crossover would be observable on approaching the phase transition in a *single liquid crystal* [21, 22]. Recent high-resolution xray scattering studies have corrected for the effect of mosaicity [50] and were qualitatively consistent with previous results with minor quantitative changes. The removal of mosaicity with a 5 T magnetic field allowed an increase in the range of the study of critical behaviour. Contrary to the Patton-Andereck prediction, the temperature dependence *in any one experiment* was still fit well by a single critical exponent.

A possible resolution of the critical exponent anisotropy was proposed by Bouwman and de Jeu [51]. By not holding the splay correlation length to $\xi_s^4 = c\xi_\perp^4$ in their fits to high-resolution x-ray structure factors, they find larger (and perhaps more realistic) estimates of the uncertainties in the correlation length exponents. Within these larger uncertainties, the spread in experimental values of critical exponents and discrepancies with the 3DXY model are less significant. Errors quoted in the recent experiments by Primak et al are significantly less [50] – yet

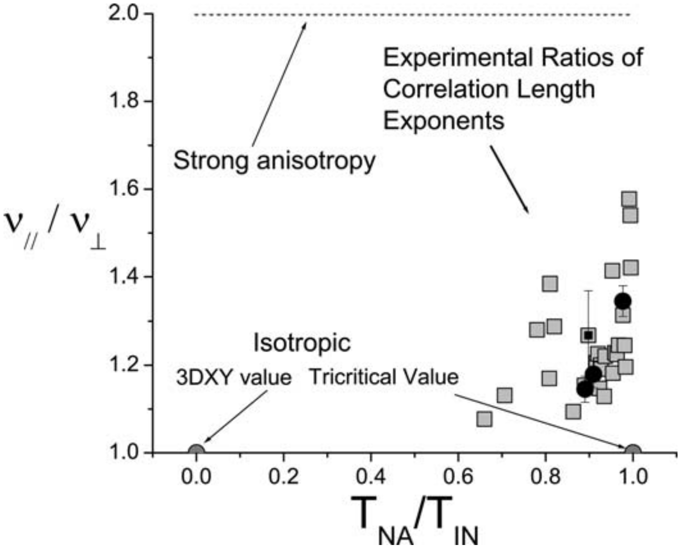

Figure 8-2. Correlation exponent anisotropy ratio $\mathsf{A}_\nu \equiv \nu_\| / \nu_\perp$ as a function of the ratio T_{NA}/T_{IN}. The grey-filled squares are values from numerous experiments (tabulated in [48]). The square with the large error bar (x-ray scattering experimental result of Bouwman and de Jeu [51]) with errors modified due to a reconsideration of the fitting procedure. The black circles with errors are from recent scattering studies with mosaicity corrections taken into account[50]. Both the 3DXY and the tricritical models predict isotropic exponents ($\mathsf{A}_\nu = 1$). Strong anisotropy would predict $\mathsf{A}_\nu = 2$

there is appreciable difference ($\mathsf{A}_\nu = 1.14 \pm 0.03 - 1.35 \pm 0.05$) in the anisotropy measured at different T_{NA}/T_{IN}.

Yet another technique, measuring ultrasonic velocity anisotropies in the vicinity of the NA transition, however, also find anisotropies consistent with crossover behaviour. Sonntag et al [52] studied the divergence of three elastic constants, the bulk compression constant *A*, the layer compression constant *B* and the bulk-layer coupling constant *C*. *B* and *C* have critical exponents that are unequal and are in between that of the 3DXY values and anisotropic scaling values.

Given the above situation with static critical exponents, it is understandable that studies of dynamical critical exponents have been fewer. Dynamical exponents were recently measured in liquid crystals whose nematic range puts them in the "crossover" region. Marinelli et al [53] found that the thermal transport critical exponents did not show any orientational dependence, i.e. they were isotropic. In addition, they found [54] the values obtained to be consistent with a dynamical model also with $n = 2$ and $d = 3$.

Much recent work has addressed the vexing question of phase transition order, reviewed in the following section. While clearly the measurements of critical exponents is predicated on the non-existence of a discontinuity, the discontinuities being argued over are small enough so as not to suppress the pre-transitional effects characteristic of a second-order phase transition. However, one cannot rule out subtle effects of one on the other.

5. EXPERIMENTS PROBING PHASE TRANSITION ORDER

Discussed in this section are the effects of fluctuations and of external fields on the phase transition. Experimentally, the NA transition is usually indistinguishable from second order [48]; however, for materials with a small nematic range, calorimetric measurements have detected a small latent heat associated with the phase change, which is interpreted as a mean-field, second-order phase transition that is driven first order by the coupling to a second, strongly fluctuating order parameter. The second order parameter is associated with a nearby transition, between the isotropic and nematic phases (IN).

One suggested way [55, 56] to compare different experimental probes of phase transition order is to express the phase transition discontinuity in terms of the dimensionless quantity $t_0 = (T_{NA} - T^*)/T^*$, where T_{NA} is the equilibrium NA transition temperature. T^* is the spinodal temperature, where the nematic phase would become unstable. One can measure T^* via almost any physical quantity by extrapolating to the temperature at which critical effects diverge. Because t_0 is positive for a first-order transition and zero in a second-order transition, it is a useful dimensionless measure of the strength of a first-order transition. One may also then use t_0 to estimate latent heats, allowing direct comparison with calorimetry experiments.

5.1 The Landau Tricritical Point and the HLM Effect

Experimental studies in the small-nematic-range limit were carried out by various groups [57–62]. Systematic measurements of the latent heat as a function of T_{NA}/T_{NI} were possible because one can tune the nematic range by mixing two almost-similar liquid crystals with slightly different aliphatic chain lengths. The alkyl-cyanobiphenyl liquid crystals "8CB" and "10CB", and alkyoxy-cyanobiphenyls "8OCB" and "10OCB" have been used extensively (8 and 10 here refer to the length of the aliphatic chain, and the series of liquid crystal with varying n is referred to as a homologous series). In the de Gennes-McMillan theory (i.e., taking only the δS-ψ coupling into account), the latent heat should vary linearly with $\delta x = x - x^*$, for small δx, where x is the mixture concentration and x^* is the concentration where the latent heat vanishes and is thus, in the context of this Landau theory, a tricritical point. By convention, x^* is known as the Landau tricritical point (LTP). Brisbin et al [57] and Thoen et al [58] showed that this is true well above x^*. Reanalyzing data [60] from mixtures of 8CB and 10CB, Anisimov et al [61] showed that the latent heat did not go to zero at the LTP but crossed over nonlinearly to a measurable, non-zero value. This indicated that something other than $\delta S - \psi$ coupling was also important, consistent with the HLM predictions. Tamblyn et al [63, 64] demonstrated a similar

Table 8-1. Latent Heats measured in pure 8CB by different techniques. A comparison of latent heats (error bars in parentheses) from Intensity fluctuation microscopy (IFM; latent heats are estimated from the measured ($t_0 = 1.2 \pm 0.1) \times 10^{-5}$ [66] and Landau parameters in [65]), Adiabatic Scanning Calorimetry (ASC; errors from [69]) and Modulated differential scanning calorimetry (MDSC; errors estimated from smaller error bar). Also listed is the molar fraction X of 10CB in 8CB-10CB (alkyl-cyanobiphenyl) mixtures at which the latent heat appears to vanish

Technique	Latent heat	Tricritical point
IFM [66]	5.25 (0.50) J/kg	NONE
ASC [60, 69]	0.0 (1.8) J/kg	$X = 0.314$
MDSC [67]	0.0 (17.0) J/kg	$X = 0.22$

dependence via capillary length (ratio of the surface tension to the latent heat) measurements on 8CB-10CB mixtures.

In addition, Anisimov et al and Cladis et al [61, 62] introduced a different technique for studying weakly first order transitions. They measured the propagation speed of a NA front after a step jump in temperature. The velocity was a linear function of the temperature jump ΔT. For second-order transitions, the front propagation speed should be proportional to $\Delta T^{1/2}$. This result implied that the NA transition was first order for all 8CB-10CB mixtures, including pure 8CB.

The above result was confirmed by Yethiraj et al [56, 66] using an optical technique that quantified intensity fluctuations in the liquid crystal. Since the intensity fluctuations in the nematic phase are caused by nematic director fluctuations, which in turn are suppressed in the smectic-A phase, this is a very sensitive probe of the phase transition. In addition, the temperature dependence of the phase transition was obtained optically by placing the sample in a well-calibrated temperature gradient. Indeed the existence of a sharp static interface is itself a qualitative indicator of first-order character. Not only was the transition in the 8CB-10CB system always first order, the strength of the discontinuity was *larger* not smaller than the HLM prediction. This result is consistent with a subsequent calculation by Herbut et al which takes into account ψ fluctuations.

Lafouresse et al [67] and Sied et al [68] have used Modulated Differential Scanning Calorimetry (MDSC) to measure latent heats as a function of concentration in two liquid crystal mixtures (8CB-10CB and 8OCB -10OCB). In both cases, they obtain results quantitatively differing from previous calorimetry results.

Experimental measurements of zero (or non-zero) latent heat should always be coupled with an estimate for experimental resolution (see Table 8-1). A recent adiabatic scanning calorimetry ("ASC") study [69] reiterates the results of an older study [58] and puts an upper bound on the NA transition in 8CB at < 2 J/kg. In the presence of relatively large impurity concentrations (~5 mole % of cyclohexane in 8CB) ASC does measure a discontinuity of 17 J/kg [70] (here the estimated errors are 5 J/kg). The stated errors in the MDSC data are large ($\approx 17\, J/kg$ as estimated from the smallest error bar on the graph) and thus consistent with both the intensity fluctuation microscopy (IFM) results of Yethiraj et al and the ASC result within errors. The ASC results are, however, clearly at odds with the IFM results of Yethiraj et al. The source of the discrepancy is unclear. It seems safe to say that the last word on phase transition order has not been spoken.

5.2 External Fields

External fields (surfaces, electric, or magnetic fields) can have an important effect on liquid crystal alignment. However, strong enough fields can also have an effect on liquid crystal phase behaviour. The work of Lelidis et al [71, 72] has demonstrated that nematic phases can be induced in a system that exhibits an isotropic and a smectic-A phase (and close in the phase diagram to the emergence of a nematic phase). Such a nematic phase has been termed "non-spontaneous" (NSN). It turns out that the NSN-A transition can also be either first or second order, and that the discontinuity can be suppressed by increasing the electric field even more! Comparable results have been found by Basappa et al [73] who were able to suppress the range of the smectic phase via an external electric field. In both cases, care had to be taken to use pulsed alternating electric fields to simultaneously prevent charge migration and prevent heating effects. The heating effects put a limit on the experimental resolution of the measurement.

Lelidis also reports [74] confirmation of the electric-field-assisted suppression of the HLM effect (predicted by Mukhopadhay et al [16]) with an important point of departure. The theory predicted a critical field of 10 T (magnetic) or 1 $\mathrm{V}/\mu\mathrm{m}$ (electric). Since this is the point when the discontinuity is completely suppressed, one would expect to see an effect for much smaller fields. However, Yethiraj et al found no trace of a field-induced suppression in magnetic fields upto 1.5 T, suggesting a minimum critical field of 33 T. This would correspond to a critical electric field of atleast $3.3\,\mathrm{V}/\mu\mathrm{m}$. The critical field reported in Ref. [74] was $20\,\mathrm{V}/\mu\mathrm{m}$, i.e. an order of magnitude higher. This result is indeed *experimentally* consistent with the earlier findings of Yethiraj et al. However, given the strength of the field required, there exists a question if the effect observed is truly the subtle HLM effect. The modified HLM theory [16] also predicts an increase in the critical field as the zero-field phase transition discontinuity (characterized, for example, by the dimensionless temperature t_0) increases. This can be achieved experimentally in a homologous mixture such as 8CB-10CB where increasing 10CB concentration increases the zero-field discontinuity. Measuring the critical electric field as a function of the concentration in mixtures might be a good test of the HLM mechanism in this case.

6. THE LANDAU-PEIERLS INSTABILITY IN SMECTICS

A smectic-A liquid crystal is expected to exhibit algebraic decay of the layer correlations rather than true long-range order [6, 7]. In x-ray scattering, the smectic Bragg peaks would be expected to be power-law singularities of the form $q_{\parallel}^{-2+\eta}$ and $q_{\perp}^{-4+\eta}$. Distinguishing between power-law singularities and "delta function" peaks broadened by diffuse scattering from acoustic modes requires an instrument with a resolution function whose wings drop off much faster than the power law/s. Als-Nielsen et al [44] found in a high-resolution x-ray diffraction study of the density wave of the smectic-A phase that the smectic-A Bragg peaks in the liquid-crystal 8OCB were indeed consistent with the predicted power-law singularity form. While a non-vanishing (i.e. a non-divergence to zero) of the layer compression modulus has been reported in second-sound measurements [75], the validity of the interpretation of the measurements has been contested via other measurements using the same technique [76]. In addition, Martinoty et al [77] found, using dynamic compression measurements, that the layer compression modulus exhibits a single power law divergence (to zero) on approaching the phase transition over 4 decades in reduced temperature.

7. SUMMARY

The nematic-smectic-A (NA) transition is one that has been studied theoretically with fluctuations being accounted for within different levels of approximation. It has also been studied experimentally by a diverse array of high-resolution techniques in laboratories around the world. While much has been understood about the transition, almost every probe of the NA transition, whether mean-field behaviour of solutes, nature of divergences and values of critical exponents or phase transition order, has met with conflicting experimental results. It appears that another generation of resolution and precision enhancement is required before the complete story is told. As remarked several years ago by deGennes and Prost [3]: “It seems that we almost understand, but not quite”.

8. ACKNOWLEDGEMENTS

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