

The re-entrant nematic and the compounds of Gray

by P. E. CLADIS

Bell Laboratories, Lucent Technologies, Murray Hill, NJ 07974, USA

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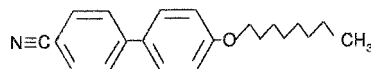
By creating and developing materials whose properties could be fully characterized, Professor George W. Gray has played a pivotal rôle in advancing our knowledge of liquid crystal states of matter. To honour him on his birthday, I briefly sketch some of my experimental results where the purity and stability of his cyanobiphenyl compounds played a crucial rôle in establishing new physical phenomena: the first re-entrant phenomenon in physics (1975, 1981) and the recent resolution of the nematic–smectic A transition order (1989, 1990). Even today, George Gray's liquid crystal materials are outstanding model systems for building physical intuition of generic non-linear, non-equilibrium problems, one of the most exciting frontiers of physics research today (1991, 1992, 1995).

My first introduction to liquid crystals (1969) was George Gray's seminal book, *Molecular Structure and the Properties of Liquid Crystals* published in 1962 [1]. While the size and complexity of the molecules that exhibited liquid crystal phases was a little daunting, a mysterious new world beckoned. In addition, Pierre Gilles de Gennes' broad interests in macroscopic physical phenomena in complex materials, drew many physicists to the world of '*la matière molle*', in particular, at that time, '*la matière molle*' exhibiting macroscopic non-linear cooperative phenomena, liquid crystals. With '*la goût de l'observation*', perhaps we could learn '*la leçon des choses*' [2].

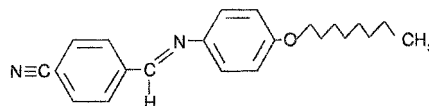
While I was in France, I never heard de Gennes discuss '*la supra*' (my thesis topic) even though he had written the best book on the subject [3]. But about a year before I left (1971), he said, 'You know, in a macroscopic sense, the nematic–smectic A transition seems similar to the normal metal–superconducting transition. On top of that, there are these new scaling ideas in phase transitions' [4]. So, off to the races.

At Bell Labs, I set up to measure the divergence in the nematic elastic constants of bend, K_3 , and twist, K_2 , that de Gennes had predicted would occur as the nematic–smectic A transition was approached [4]. The material I used is known by many names but the one I used was CBOOA (figure 1). It was a cyano-compound with a Schiff's base linkage like the notorious room temperature nematic, MBBA (methoxybenzilidene butylaniline).

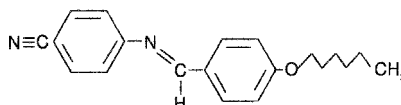
Bill McMillan was the first to measure critical exponents at the nematic–smectic A transition. He did this before he left Bell Labs in 1972 [5], the year I arrived.



80CB: 4-cyano-4'-octyloxybiphenyl



CBOOA: N-p-cyanobenzylidene p-octyloxyaniline



HBAB: p-hexyloxybenzylidene-p-aminobenzonitrile

Figure 1. The cyano compounds that have played an important rôle in re-entrant phenomena in liquid crystals.

The material he selected for his study was CBOOA. He may even have synthesized it (once) at Bell Labs. McMillan had a theory that said that one needed a large nematic range to approach second order behaviour at this transition. He introduced the parameter that we now call the McMillan number, $M = T_{NA}/T_{NI}$ where NA refers to the nematic–smectic A and NI to the nematic–isotropic transition temperatures (in K). As $M \rightarrow 0.88$, he predicted that the NA transition became more second

order because director orientational fluctuations were calmer the further the liquid crystal was from the NI transition. But, the exponents he obtained from his X-ray measurements of the structure factor for smectic A fluctuations in CBOOA ($M \sim 0.93$) were not in any known universal class. Not only that, he found two different ones: one for the coherence length, ξ_{\parallel} and another for ξ_{\perp} where \parallel and \perp refer to the director.

I tried to do ‘better’ by measuring $K_3 \sim \xi_{\parallel}$ and $K_2 \sim \xi_{\perp}^2/\xi_{\parallel}$ for CBOOA and found even *more* non-universal exponents [6]. Everyone was very puzzled by these results. Subsequent more refined measurements using fits to more sophisticated functional forms also found different and non-universal exponents for ξ_{\parallel} and ξ_{\perp} —even on the compounds of Gray, well-known for their temperature stability and purity [7]. While we could qualitatively verify de Gennes’ and McMillan’s predictions, the numbers were not working out. Maybe there was something interesting to be learned from ‘*la leçon des choses*’?

How to explain all these exponents? I started studying mixtures with the goal of obtaining ‘proof’ that this transition had to be first order—at least in CBOOA. My idea was to study controlled ‘dirty’ systems [8]. One of the compounds I mixed with CBOOA was HBAB (figure 1: another Schiff’s base!).

HBAB was in my lab because it had been reported that flow alignment [9] broke down in this material [10] and it was available in large quantities. Françoise Brochard explained [11] that this could indeed happen if one of the nematic viscous coefficients, α_3 , changed sign because of smectic A fluctuations. The fascinating results Sergio Torza and I found using CBOOA and HBAB are another story [12]. However, when I used HBAB for my ‘controlled studies’ of CBOOA mixtures, I discovered the re-entrant nematic transition in CBOOA/HBAB mixtures [13].

The observation with decreasing temperature was: nematic, then smectic A, then, nematic again (e.g. figure 2). The nematic phase re-entered at a lower temperature than the more ordered smectic A state. As the concentration of a shorter isomeric compound (HBAB in this case) increased, the nematic range became broader. While T_{NA} decreased, T_{NI} did not change much; the McMillan number became smaller. However, as $M \rightarrow 0.88$, rather than becoming more second order, the smectic A phase disappeared [13]. I was reminded of the old argument for why there could not be an Ehrenfest-type second order phase transition [14].

After reassuring me that our notion of phase transitions had advanced *considerably* since those early days, Bert Halperin told me about their novel idea, the HLM theory, for why transitions were first order for superconductors and smectic A’s [15]. While we knew that

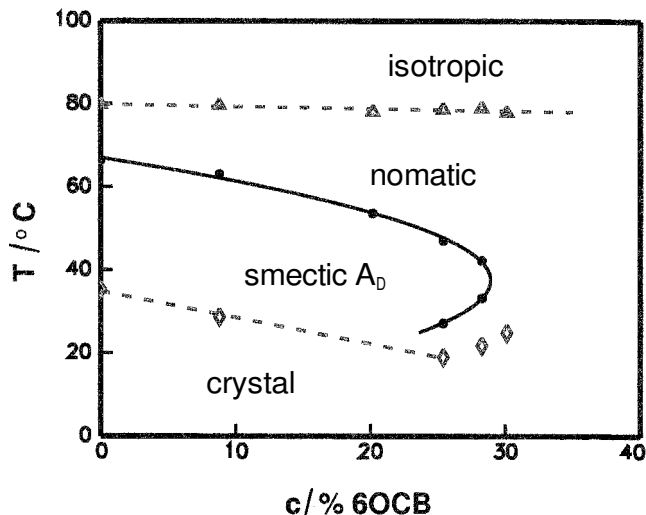
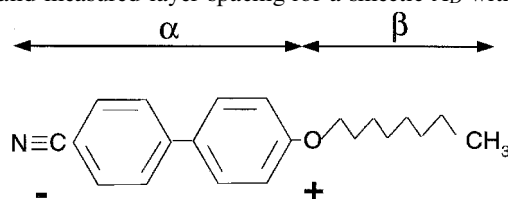


Figure 2. The re-entrant phase diagram of 60CB and 80CB mixtures [23].

smectic A layering fluctuations suppressed transverse director fluctuations (leading to divergences in the twist, K_2 , and bend, K_3 , elastic constants) [4], when they averaged over the director fluctuations, assuming a constant value ψ for the smectic A order parameter (a mean field approximation), they found a gap at long wavelengths in the spectrum of transverse director fluctuations [15]. This gap, which depended on ψ , resulted in a cubic term ($\psi^2|\psi$) appearing in the effective free energy expansion in powers of ψ , making the NA transition necessarily first order [16]. But, it could be an immeasurably small effect.

It took us [17] about 15 years to find evidence supporting the existence of the HLM cubic term [15]. That was because we had first to invent a new dynamic way (front propagation) to test phase transition order [18]. This collaboration involved many talented colleagues, from many different countries and many different fields. (International and interdisciplinary collaborations are one of the many advantages of doing research in liquid crystals.) While these results are not directly related to our quest for understanding re-entrant behaviour, I mention it at this celebration because it was our trust in the purity and stability of the cyanobiphenyl compounds of Gray that was crucial in helping us resolve this very old puzzle of the NA phase transition.

In 1975, I wanted to understand these unusual non-linear phase diagrams (e.g. figure 2). Up to then, it was assumed that the smectic A layer spacing was always approximately the molecular length. A surprising result was that the smectic A layer spacing in 8CB was about 1.5 times *larger* than the molecular length. The, then, very novel material, 8CB (4-cyano-4'-octylbiphenyl) [19] was the first room temperature smectic A. It was

Table. Predicted and measured layer spacing for a smectic A_D with overlapped dimers.

Compound	Cyano aromatic moiety: $\alpha/\text{\AA}$	Aliphatic chain length: $\beta/\text{\AA}$	Total length: $\alpha + \beta/\text{\AA}$	Model length: $\alpha + 2\beta/\text{\AA}$	Measured length/ \AA
CBOOA	16.0	10.4	26.4	36.8	36.3
HBAB	16.0	8.2	24.2	—	—
8OCB	13.9	9.2	23.1	32.3	30.8

made by George Gray. While Gray and Lydon examined many molecular associations [19], the one I thought could destabilize smectic A layering was one (that they did not consider) where electronic interactions favoured aromatic moieties forming overlapped pairs [13]. Later we called this type of smectic A phase, smectic A_D. As it was not clear at that time how re-entrant phenomena could be related to 8CB (not widely available until about 1977), the sensible strategy seemed to be to obtain more information from compounds available to us.

In 1977, we studied mixtures of cyano-Schiff's base compounds, synthesized by Gary Taylor at Bell Labs, under pressure [20]. We found that there was a maximum pressure for stability of the smectic A phase. Even in a pure compound, the nematic–smectic A–re-entrant nematic phase sequence could be observed with decreasing temperature and increasing pressure. With the addition of a shorter homologue, this maximum pressure decreased [20].

About this time, Leadbetter *et al.* [21] also concluded that a similar overlapped dimer was the likely form for molecular associations in cyanobiphenyl compounds. Their conclusion was based on evidence found from neutron diffraction of selectively deuteriated samples of 8CB which has (so far) not exhibited re-entrant behaviour [22].

Daniel Guillon, Jim Stamatoff and I then measured layer spacings of compounds exhibiting re-entrant behaviour [23]. The evidence was strongly in favour of a smectic A layer structure formed of overlapping aromatic moieties (table). We began calling the smectic A phase that appeared between the two nematic phases, smectic A_D; D stood for dimers. We also sketched pictures of what it might mean on a microscopic length scale [24]. From these sketches, it seemed clear that both electronic and steric features of these molecular associations played a significant role in the re-entrant phenomenon [25]. They could even lead to a state

resembling smectic C (accounting for the 19°A line found by Daniel Guillon) [24]. John Goodby and Tom Leslie later showed that, indeed, remarkable changes in phase sequences occurred when specific electronic features were controlled on a molecular scale [26].

Eventually we concluded [13] that smectic A_D was a statistical ensemble of dimers and single molecules [27]. X-ray diffraction measurements of smectic A_D showed that, as the layer spacing decreased (interpreted to mean that the overlapped pair population also decreased) T_{NA} , as well as the maximum pressure at which smectic A_D was stable, increased [13].

In 1981, I summarized these results on mixtures of 6OCB and 8OCB [13], the alkoxy-cyanobiphenyl compounds of Gray showing re-entrant behaviour [23], and analysed them in terms of dimer and monomer lengths. The conclusion from this analysis was that as the layer spacing approached that of an ensemble of overlapped pairs, the smectic A_D phase was squeezed out. Furthermore, when the layer spacing approached a value consistent with a population of mostly disassociated single molecules (obtained by mixing 8OCB with 40:8 (butyloxybenzylidene octylaniline) which has a smectic A layer spacing close to its molecular length), the nematic phase no longer occurred [13].

To answer the question, 'What is *la leçon des choses*?', Nihat Berker and collaborators developed a 'frustration' theory of three body dipolar interactions [28]. Roughly speaking, frustration indicates the presence of a wide variety of conflicting goals arising from random interactions in many body systems [29]. It can lead to a non-ergodic state known as a spin-glass where different regions of phase space become irretrievably separated by energy barriers. In the smectic A_D case, Berker and collaborators investigated a two-body dipolar potential with ferroelectric and antiferroelectric interactions, and then considered the effect on a third dipole. The dipoles are oriented parallel to the layer normal. When dipolar

forces between two particles cancel (which we would associate with completely overlapped aromatic moieties in cyano compounds), a third dipole experiences no force and is free to permeate (diffuse) from layer to layer ‘frustrating’ smectic order. In this situation, the nematic re-enters. On the other hand, a population of triplets (with a layer spacing between that of a dimer and a single molecular length) stabilizes smectic order through short-range dipolar interactions. While both smectic A_D and the re-entrant nematic are frustrated, they escape being non-ergodic because they are liquids in the usual sense. Indeed, Berker and co-workers refer to their theory as a spin-gas theory rather than a spin-glass theory [28]. By introducing the notion of ‘permeation minima’, which they liken to notches that stabilize a particular triplet configuration, their theory has successfully accounted for multiple re-entrance, as well as re-entrance involving smectic C phases. Their theory is particularly satisfying because one can relate their various frustrated and unfrustrated states to intuitively acceptable (and observable) molecular associations based on knowledge of molecular structure.

I believe that many of the breakthroughs in our understanding of re-entrant nematic phenomena resulted from our being able to trust what we observed and measured. We could build on information obtained from observations because of the robustness of the liquid crystal materials we had used. This has been especially the case for the cyanobiphenyl compounds of Gray. Thank you George Gray, from all physicists. Your compounds not only open doors on to new physics, they give us confidence to pass through these doors.

As cyano-compounds are so well characterized, they are excellent model systems to build intuition and understanding of novel physical phenomena, in particular now for me, novel dynamic phenomena [30]. Liquid crystals are emerging as a kind of analogue ‘computer’ that solves complicated coupled non-linear PDEs faster—with instant graphics—than our fastest solid state silicon machines. At the frontiers of fundamental physics research, liquid crystals are still adding to their formidable track record for shedding a new glow on dreams of human beings and silicon machines. For sure, they have given an invigorating, perhaps in some cases an intoxicating, flavour to ‘*la goût de l’observation*’.

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