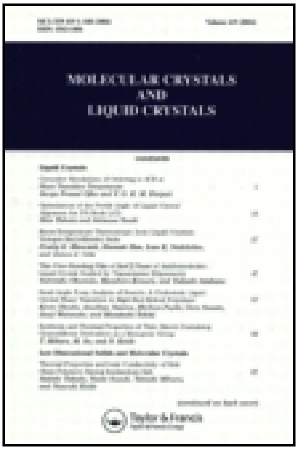

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A One Hundred Year Perspective of the Reentrant Nematic Phase

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A One Hundred Year Perspective of the Reentrant Nematic Phase

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Since the discovery of liquid crystals one hundred years ago, reentrant phase transitions have transformed from being isolated curiosities to an established phenomenon. A significant influence for this change in point of view, has been the almost overnight discovery of the many reentrant transitions in liquid crystals. In this review, I survey some of the interesting results discovered by different groups studying the reentrant nematic phase since its discovery making contact with current theories whenever possible.

To put the reentrant nematic in the context of current understanding and to provide a historical perspective of this phenomenon, I summarize some reentrant transitions in other systems. In particular, I discuss the ferroelectric transition in the molecular crystal, Rochelle salt, because it may be the first observed example of a reentrant transition. Again, whenever possible, similarities and differences to the liquid crystal case are discussed.

I. INTRODUCTION

Apart from the existence of the various liquid crystal states, one of the most surprising discoveries this state of matter has shown is, with decreasing temperature, the remarkable phase transition sequence: nematic–smectic A–reentrant nematic.[1] Although subtle differences have been noted in its short range structure and transport properties, the reentrant nematic phase is identical in its long-range physical properties with the higher temperature nematic phase. This is in contrast to systems that also show reentrant behavior for a particular set of parameters[2] because of the onset of long-range order at the reentrant transition.

To prepare this article, I made a search of all papers with the word reentrant (or re( )entrant) in the title since 1969. I was astonished to learn that since about 1977, there were more than 1000 such papers. It has obviously not been possible for me to read most of these papers (of which only 72 also had "liquid crystal" in the title) but I learned an interesting fact that I believe is appropriate to mention in this celebration review of the 100th anniversary of the discovery of liquid crystals. I learned that liquid crystals provide useful paradigms for science. In particular, they have changed the way we think about phase transitions.

Before 1977, 211 papers were retrieved with the word reentrant in their titles. None of the papers concern phase transitions and appear to use the word in the common English sense as a technical term in software design, microwave cavities, housings for lenses and semiconductors, and in electronics. The first known case of reentrance in phase transitions that we found was observed in 1921 by Valasek[3] who discovered that Rochelle salt was ferroelectric between 24°C and −18°C.

The use of "reentrance" to phase transitions dates from about 1977 when the term was applied to the superconducting transition.[2] Inspired by de Gennes' analogy between the normal metal superconducting transition and the nematic smectic A transition,[4] we applied it to the reentrant transition in liquid crystals.[5] It has since become a generic term.

Of the 1052 titles employing "reentrant" or "re( )entrant" since 1977, about 669 are related to reentrance in magnetic superconductors. Of the remaining papers, 183 are related to the reentrant transition in spin glasses and/or magnetism and 72 to reentrant transitions in liquid crystals. A few of the topics, along with more recent references, in the last set of 128 titles are listed below:

—Reentrant behavior in geological substrates[6]
—Phase transitions of krypton on graphite[7]
—Re-entrant corners on the surface of twinned crystals[8]
—Wetting transitions[9]
—Highly polarized liquid ^{3}He as a function of pressure[10]
—Swelling transitions in gels[11]
—Cardiac arrythmias[12]
—The knights move in chess.[13]

The earliest theoretical demonstration of reentrant behavior that we found was given by Vaks et al. in 1965.[14] In their paper, they caution that the phase diagram they had calculated was unusual. They gave a reference[15] to Rochelle salt as being the rare case where it had been observed. Judging from the number of reentrant references since 1977, reentrant phase transitions are now an established phenomenon.

Certainly for liquid crystals, every year since 1979, the study of reentrant phases becomes broader faster than it becomes deeper. It is therefore difficult to give an elegant and closed representation of the topic as a whole. In the next section of this paper, I list a few of the many interesting results that have been discovered by different groups studying reentrant transitions in liquid crystals. I tried to show, where possible, how the various experimental results fit into current theories.

Frustration has emerged as a key concept in describing reentrant transitions. The use of the word *frustration* to condensed phases was introduced by G. Toulouse after a remark of P. W. Anderson. Roughly speaking, it indicates the presence of a wide variety of conflicting goals arising from random interactions in a many body system.[16] The first model Hamiltonian to reveal this was the Ising Hamiltonian of N spins at N sites with random nearest neighbor interactions. The statistical mechanics of this system revealed a sharp transition in the $N \rightarrow \infty$ limit to a non-ergodic state, the spin glass state, where different regions of phase space become irretrievably separated by energy barriers. As the temperature is lowered, these regions proliferate.

Frustration is also found in Ising systems with ferromagnetic and antiferromagnetic competing interactions on a square lattice. When competing next nearest neighbor interactions are introduced, as for example in the early paper by Vaks et al.,[13] reentrant transitions result. It typically occurs for only a narrow range of coupling constants.

In liquid crystals, the reentrant transition that has been most investigated is the nematic–smectic A transition. At this transition, a uniaxial liquid phase (nematic) transforms to a phase with layers parallel to the direction of orientational order (smectic A). In the plane of the layers, a system in the smectic A phase is fluid.

The Hamiltonian that has been investigated to explain reentrant transitions in polar compounds consists of a two particle dipolar potential that has competing ferroelectric and antiferroelectric interactions.[17–19] The dipoles are oriented parallel to the layer normal. The system is analyzed in terms of three dipoles or triplets. When dipolar forces between two cancel, the third dipole experiences no force. It is free to permeate from layer to layer "frustrating" smectic order. However, by allowing displacements of three dipoles relative to each other in the layering direction, a population of triplets is generated that has a net short range dipole. They interact with neighboring triplets within a plane via short range antiferroelectric or ferroelectric interactions thus stabilizing the layered structure.[17-19] The energy fluctuations associated with an ensemble of triplets is evaluated. If an Ising criterion is satisfied, it is concluded that the ensemble stabilizes a layer structure. If the criteria cannot be satisfied, it is concluded that a disordered state (the nematic) prevails.

Both the smectic A and the reentrant nematic are frustrated but they escape being non-ergodic because they are liquids in the usual sense. Indeed, Berker et al.[17-19] refer to their theory as a spin-gas theory as opposed to a spin-glass theory. The current challenge is to relate the various states that emerge from collecting the statistics of this model to a microscopic picture appropriate to liquid crystals.

In this paper, I concentrate on simple reentrant behavior and how the frustration idea may be particularly valuable in organizing the vast body of experimental lore, described in Section II, that has emerged in studying this transition.. In order to relate some specific features of the frustration theory to the many experimental results, I give a simplified version of it in Section IIA. To put the reentrant nematic in a context of recent advances in our understanding of this phase transition, I summarize in Section III some reentrant transitions in other systems noting similarities and differences, to the liquid crystal case as they emerge.

I was particularly fascinated by the case of Rochelle salt (discussed in Section IIIA) because its ferroelectric phase may be the first example of a reentrant transition ever observed. The low temperature paraelectric state of Rochelle salt may be a spin glass. Its phase diagram is then not truly reentrant because the low temperature phase would not be identical to the high temperature phase as it is in the case of the reentrant nematic, for example. Because I found it helpful (and amusing) to see similar features to reentrant phase transition theories in other systems, I discuss again in this section the frustration theory of Berker and his collaborators.[17-19]

In 1986, Hinov[20] published a useful bibliography of 87 articles in print between 1977 and 1984 on reentrant transitions in liquid crystals at atmospheric pressure. We note that many of the papers he collected did not turn up in our search. Many papers, even after 1977 without reentrant in their title were not retrieved by our search directly but through discussion with colleagues and following references cited in the articles that did turn up.

II. SIMPLE REENTRANT BEHAVIOR IN LIQUID CRYSTALS

In 1975, we observed the reentrant nematic in a mixture of CBOOA (cyanobenzilidene butylaniline) and HBAB (hexyloxybenzilidene amino

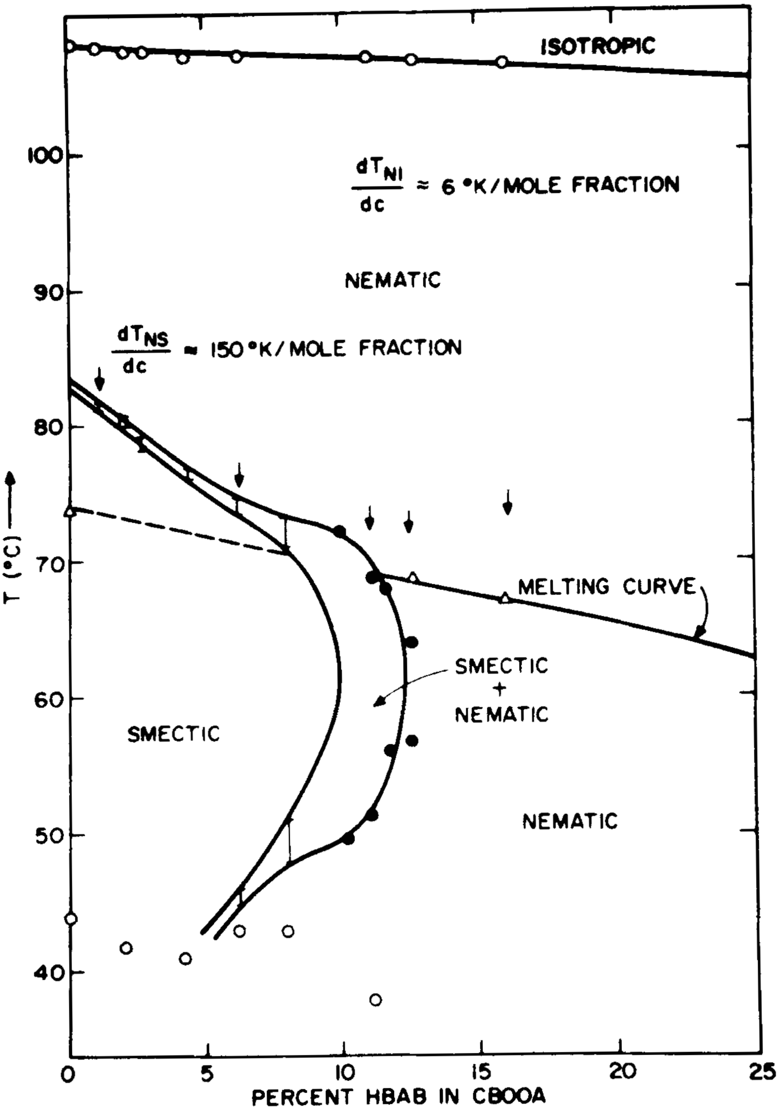


FIGURE 1 The phase diagram of the first reentrant nematic phase in mixtures. (P. E. Cladis, *Phys. Rev. Lett.*, **35**, 48 (1975).)

benzonitrile).[1] It was not called reentrant then (Figure 1). After discussing this result with Bert Halperin, I gave as a qualitative description of the phase transition curve bounding the smectic A phase: $c = c_o + \beta(T_{NS} - T_o)^2$. c refers to the concentration of HBAB and T_{NS} is the nematic–smectic A phase transition temperature. From measurements of the elastic constant of bend and the observations of the NA transition in an applied magnetic field, I concluded that the two nematic phases were identical but, the "real" shape of the reentrant curve as a function of concentration is seen (Figure 1) to be only approximately parabolic. On the other hand, a parabolic form for the phase transition line accounted for the doubling of the exponents of the bend elastic constant of CBOOA doped with the ortho-isomer of MBBA (methoxy butylaniline),[21] previously observed. These mixtures, however, are not reentrant.

In 1979, Pershan and Prost[22] found a physical interpretation of the parabolic form. They pointed out that such a shape for the transition line was consistent with an optimum density for the smectic A phase. Their theory has turned out to be a useful, but not perfect, description of the nature of the reentrant nematic–smectic A phase transition.

In 1975, physicists were only just becoming aware that the layer spacing of the smectic A phase of cyano-compounds was larger but not an integral multiple of the molecular length. Indeed, it has since these early days turned out to be anywhere from one to two times the molecular length depending on the compound. In cyano compounds with two aromatic rings, it is about 1.4 times the molecular length.[23] It seemed reasonable, therefore, to propose that this discrepancy represented a clue to the occurrence of this, then unusual phase diagram (Figure 1).[1] This type of smectic A phase has been called an incommensurate smectic A phase, denoted A_D, with D standing for dimers. We will see, in Section IIB, the motivation behind the dimer idea. A smectic A phase with a layer spacing (more or less) commensurate with a molecular length is called smectic A_1.

Prost and Barois[24] constructed a Landau theory of two coupled order parameters. A length was associated with each order parameter. For one, it was the molecular length and for the other a dipolar length. In their theory, the layer spacing in the A_D phase was determined by competition between the two lengths and the reentrant nematic phase was contained in their theory.

A spin-gas microscopic theory has been developed by Berker and collaborators.[17–19] Frustration has turned out to be a useful concept to describe reentrant transitions, particularly multiple reentrance. We discuss their frustration scenario next.

A. Frustration and competing interactions

In a mean field strategy with competing interactions, the system democratically chooses a compromise state in which all members of the system are a little bit unhappy. In contrast, in the frustration strategy, the system chooses a configuration where all members are locally satisfied. When the locally satisfied members are brought into contact, the magnitude in the energy fluctuations are monitored. After the locally satisfied regions are brought into contact, the magnitude in the energy fluctuations are monitored. If these are large, the system is unfrustrated and orders to find the optimum configuration. If these are small, no solution exists and the system is called *frustrated*.[16]

Entropy is important for stabilizing many body systems that have a large number of degenerate states. Members of a frustrated system are not locked into a single state and so contribute to the entropy but not the symmetry. In reviewing the Berker theory, the picture that emerges is that the reentrant nematic in polar compounds is a frustrated smectic A (no solution). It is saved from being non-ergodic because it is a 3-d liquid. We will see in Section III, in a 2-d Ising context, the structure of the smectic phases they describe are frustrated and the nematic phase is a disordered phase.

Berker and colleagues[17–19] use a Hamiltonian of the form:

$$V_{12} = \frac{[A\mathbf{s}_1\cdot\mathbf{s}_2 - 3B(\mathbf{s}_1\cdot\mathbf{r}_{12})(\mathbf{s}_2\cdot\mathbf{r}_{12})]}{r_{12}^3} \tag{1}$$

A well oriented smectic or nematic is assumed so $s_i = \pm 1$. When $A = B$, the interactions are purely dipolar. When $B < A$, antiferroelectric order is favored and when $B > A$, ferroelectric interactions are favored.

Dipoles, represented by $\mathbf{s}_i$, are oriented parallel to a layer normal. In order to set up their ensemble of triplets, notches are installed in each layer. The notches allow them to consider configurations where dipoles are displaced on atomic length scales out of the layer. In their scheme, when two dipoles are in an anti-ferroelectric orientation and in the same notch, there is a near cancellation of forces between the "dimer" and the third member of the triplet that is now free to permeate parallel to the layers. This triplet does not stabilize a layered structure. Triplets that are displaced relative to each other parallel to $\mathbf{s}_i$ have a net dipole and so can stabilize a layered structure through short range ferroelectric or antiferroelectric interactions.

The variance in the energy is monitored and ranked as strongest, intermediate and weakest. A criterion from the distorted Ising system is invoked. If this can be satisfied, then a layered structure can be stabilized. When the sign of the strongest and intermediate interactions are the same, the dominant interaction stabilizing the layer is ferroelectric, associated with smectic A_1 and when opposite, it is antiferroelectric, associated with A_D. If the criterion cannot be satisfied, then the nematic state (a disordered state) results.

By following the statistics of the different classes of configurations as A and B in Equation (1) and the number of notches are varied, a rich variety of reentrant behavior is predicted.[17-19] For example, they find quadrupally reentrant behavior typically for $1.856 < B/A < 1.896$ when there are four permeation minima (notches) and $1.445 < B/A < 1.466$ when there are five.

It is interesting to note that in 2-d Ising models with antiferromagnetic and ferromagnetic interactions, a disordered state always occurs on the phase diagram between the antiferromagnetic and ferromagnetic states. Sometimes the transition to the disordered state is reentrant and sometimes it is not. In 3-d, however, a disordered state need not separate the ferromagnetic from the antiferromagnetic states. For example, Hui[25] recently obtained on a three dimensional anti-metamagnet lattice a second order reentrant transition between the ferromagnetic and the antiferromagnetic states.

In the next section, we attempt to relate these ideas to simple molecular models relevant to reentrant transitions in polar liquid crystals. A complete theory has not yet emerged but frustration theory has the potential to account for many of the observed features of the reentrant nematic transition. Presumably this will evolve as next nearest neighbor interactions and orientational order are also included in the theory.

B. The dimer scenario for reentrance

Figure 2 summarizes a molecular paradigm constructed to account for the reentrant nematic phase.[26] Exploiting the large dipole peculiar to cyano compounds (Figure 2a), this model accounts for the incommensurate layer spacing when two molecules form a dimer as shown in Figure 2b. It was reasoned that in this way, the dipolar forces stabilizing the layered phase would be weakened, and eventually collapse, as the dimer population increased. With no force to stabilize the layer structure, the smectic A phase cedes to the nematic phase (Figure 2c). As mentioned in Section IIA, this corresponds to a frustrated triplet. This is a special triplet composed of a dimer, an antiferroelectric pair stabilized in the same notch, and a monomer free to permeate parallel to the layers.

In Figure 2c, the molecular picture of the low temperature A phase was considered to be composed of completely interdigitated molecules. The layer spacing of the interdigitated structure is equal to the monomer length but it is not composed of monomers. It is a com-

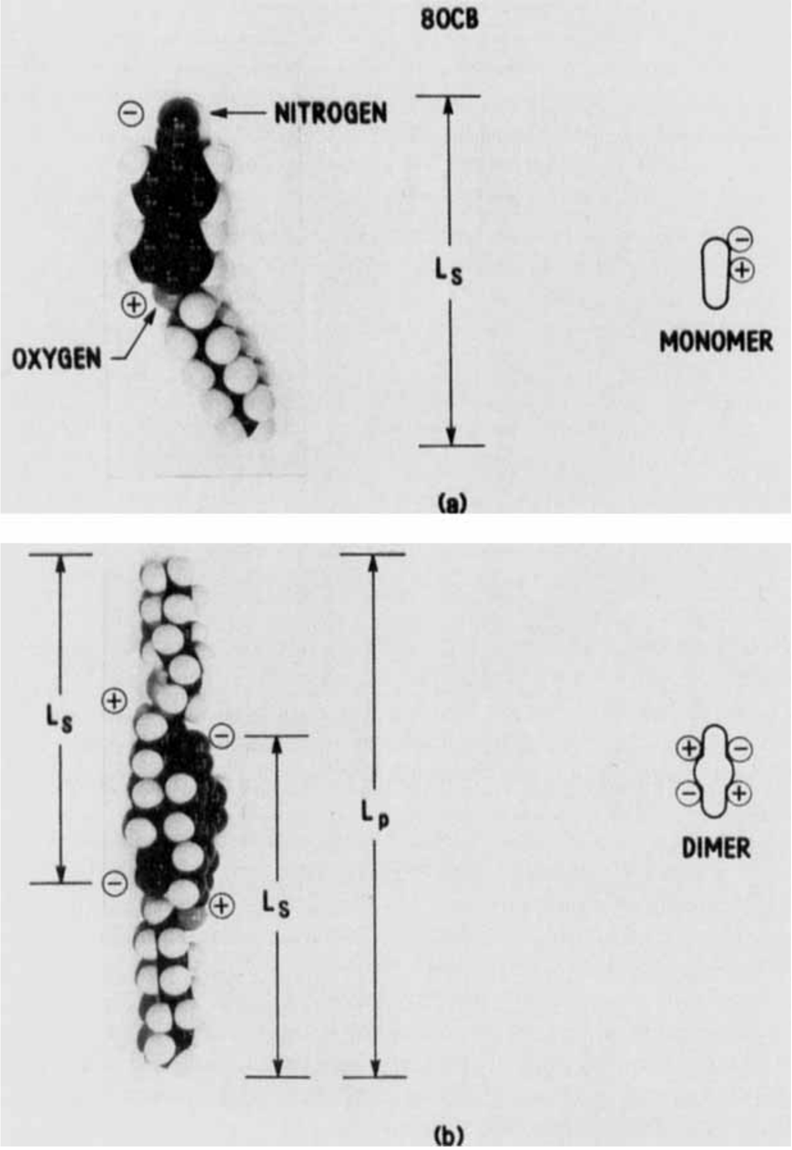
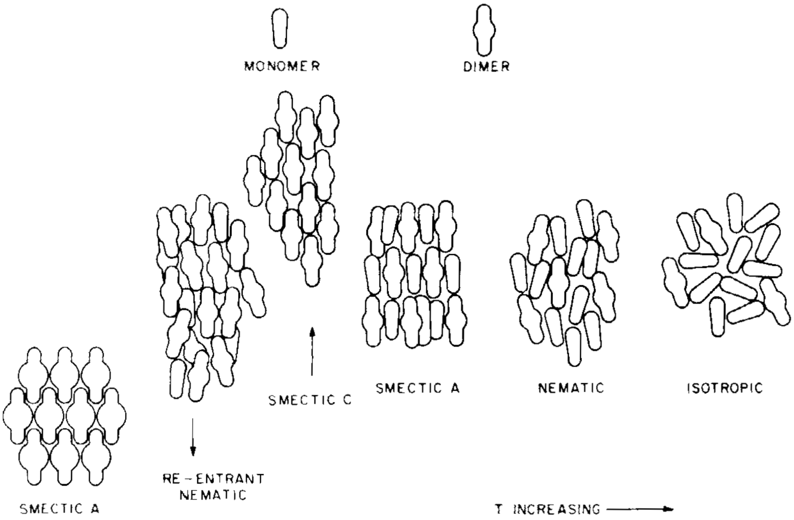


FIGURE 2 (a) A molecular model of a generic polar compound, 8OCB. A dipole is associated with the aromatic section of the molecule so that the layer spacing of the smectic A_D phase was believed to be a consequence of the formation of partially overlapped dimers (b). (a and b from P. E. Cladis, R. K. Bogardus and S. Aadsen, *Phys. Rev.*, **18**, 2292 (1978).) (c) A molecular paradigm of the reentrant scenario. (c from P. E. Cladis, S. Kobayshi and N. Matsuura, *Butsuri*, **37**, 226 (1982).) The smectic C phase can occur with decreasing temperatures to relieve the unfavorable packing imposed on overlapped dimers by the smectic A phase.



(c)

FIGURE 2 (*continued*)

pletely interdigitated structure, with all molecules on one layer oriented the same way. The dipoles in each layer are opposite to the "ferroelectric" ordering of layers above and below it. It is a more ordered structure than the ferroelectric A_1 structure of the frustration theory where the ferroelectric ordering is uncorrelated from layer to layer.

Although it looks like the frustration model in one layer, it represents nearest neighbor interactions that are ferroelectric and nearest neighbor interactions that are antiferroelectric. This is, therefore, not a frustrated structure. It is stabilized by next nearest neighbor interaction. Presumably, once density, or steric, and next nearest neighbor interactions are included, the A_1 phase of both the frustration theory and the molecular picture will agree in more detail. Owing to its compact and unfrustrated structure, it seems unlikely that it will be destabilized by a reentrant nematic or an A_D phase as the A_1 smectic can be in the frustration scenario.[19]

The smectic A_D phase is associated with a triplet with antiferroelectric short range interactions. Three dipoles, two parallel and one antiparallel, are stabilized in three different neighboring notches.[18] By allowing atomic permeation to three separate levels, dipole forces do not cancel and a layer structure can be stabilized. Within a layer, triplets interact through short range antiferroelectric interactions. If they sustain long-range order within a layer the smectic A_D is stabilized.

Entropy stabilizes the nematic phase relative to a lower and a higher temperature smectic phase. It is only at T = 0, where there is no entropy, that the total energy of the nematic, A_D and A_1 are equal. This can be seen as a feature in most of the theoretical phase diagrams.[17-19] The bicritical point, the intersection of A_D, A_1 and the reentrant nematic transition lines is at T = 0. (See Section IIID1).

A smectic-A phase of monomers will simply be called A. In frustration theory, it is a special case of A_D with purely dipolar interactions: A = B in Equation (1). A phase transition is not expected to occur between a smectic A composed of monomers, as for example stabilized by symmetric molecules, and smectic A_D. This seems to be because "symmetric" molecules are modeled as being purely dipolar in their interactions.

Several observations of mixtures on polar and non-polar com-

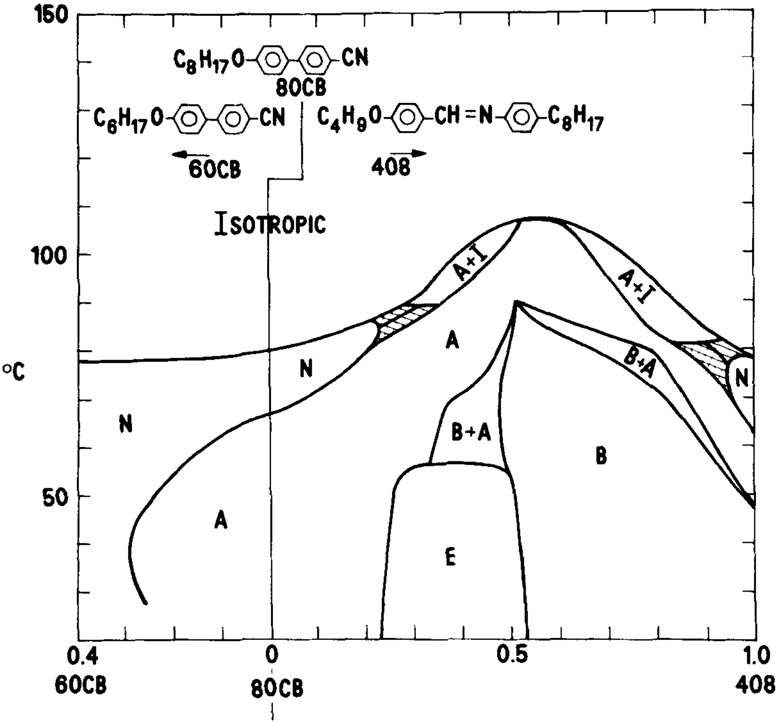


FIGURE 3 Phase diagram of 8OCB with 6OCB and 4O.8. 4O.8 forms commensurate smectic phases. From x-ray diffraction measurements the layer spacing is consistent with a commensurate phase for more than 50% 4O.8 in 8OCB. In contrast, the 6OCB/8OCB mixture exhibits an incommensurate A phase, A_D. No phase transition intervenes between these two smectic phases. (P. E. Cladis, *Mol. Cryst. Liq. Cryst.*, **67**, 177 (1981).)

pounds in two-ring compounds have shed light on the stability of the monomer A phase relative to an A_D phase.[27-30] Some of these observations are complicated by a miscibility gap.[29,30] We therefore discuss first the simplest case (Figure 3) where there is no miscibility gap: mixtures of 8OCB (cyano-octyloxybiphenyl) and 4O.8 (butyloxybenzilidene octylaniline).[27]

8OCB exhibits an incommensurate A phase and 4O.8, a commensurate A phase. By mixing one compound with the other, an incommensurate A phase is observed for 8OCB rich mixtures and a commensurate A phase is observed for 4O.8 rich mixtures. X-ray diffraction measurements of the layer spacing show the onset of the monomer regime to be at ~50% 4O.8 in 8OCB. With increasing concentration of 4O.8 in 8OCB, the layer spacing changes in a smooth and continuous way from an incommensurate value to a length compatible with a mixture of single molecules for the 50% and greater concentrations. A phase transition line is not observed.

This result[27,28] is consistent with the description that the layer spacing in the A_D phase is a statistical object.[17-19] It may be anywhere between that associated with a single molecular length and a length associated with the A_D triplet. A similar idea has been proposed by Guillon and Skoulios[28] in a two-state Boltzmann theory to account for their observations. These authors use a different model for the dimer than shown in Figure 2b.

In their scheme, the dimer is a head to head arrangement not an overlapped pair.[28] The layer spacing observed in the A_D phase is thus a combination of monomers and commensurate dimers. When the triplet state is composed of this pair and a monomer, the average molecular length will be close to 1.5 times the molecular length. With overlapped dimers, this number is closer to 1.2. Given the complexity of the molecules, it seems possible that both kinds of associations may occur, opening the door to multiple reentrance.

A previous study by Engelen et al.[29] on mixtures of polar and nonpolar compounds, observed a miscibility gap between two dimer smectic A phases. On one side of the miscibility gap, the dimer A phase eventually transformed to a monomer A phase without revealing a phase transition. Because of the temperature enhancement of the dimer phase that eventually became a monomer A phase, they concluded that a "virtual" phase transition could occur between a monomer phase and a dimer phase. But the monomer phase would have to be the high temperature smectic phase, not the low temperature one. Their comment provides a strong argument against the low temperature A phase being composed of monomers.

The shape of the miscibility gap is interesting in these studies.[29,30] In some mixtures it is reentrant on both sides of the miscibility gap. This raises a serious question concerning the universality of the parabolic shape of the phase transition line.

In the theory of Prost et al.[24] the structure of the A_1 phase is depicted as composed of disassociated monomers. This is not an essential element of their theory which is not microscopic. Their low temperature A phase can just as well be interpreted as a phase where three or more molecules are correlated as in the frustration theory.[17-19]

A molecular picture of the ordered A phase could be the one of overlapped cores and chains (as sketched in Figure 2c).[26] But again, taking into account the statistical nature of frustration theory, the lines between the different pairs do not exist. They are only a guide for the mind's eye.

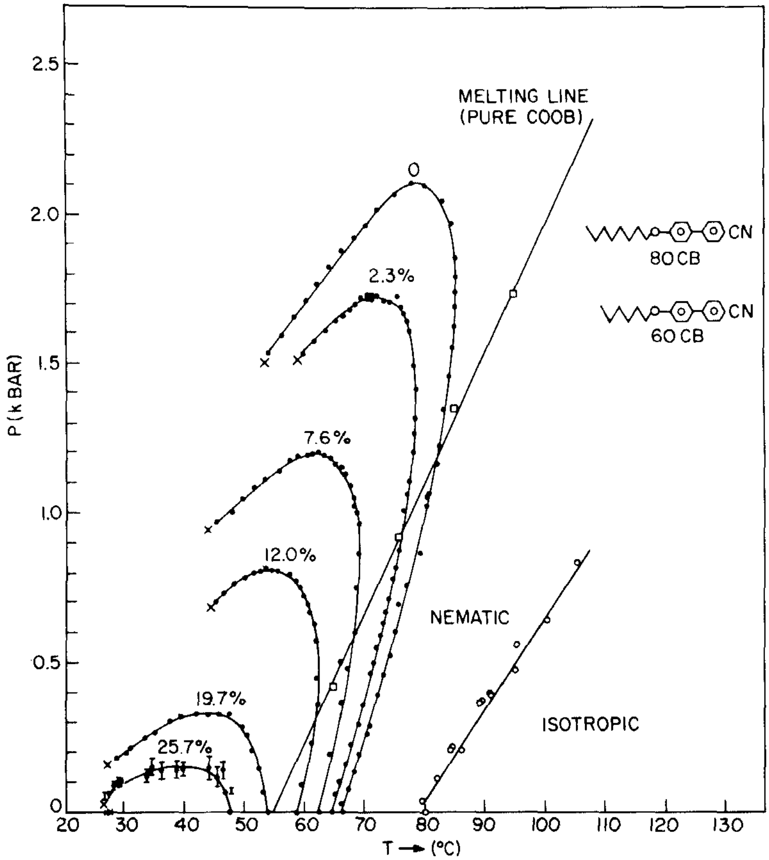
Indekeu and Berker note that correlated triplets can associate in an extended network, forming a weak molecular polymer, in the plane of the layers.[18] This takes us back to the monomer–dimer picture with triplets replacing monomers and the whole scenario starts again, but with a difference: now the polymer structure of the layers is believed to prevent free permeation out of the layers. This leads to the possibility of stabilizing an A_D phase below an A_1 phase.

C. The establishment of reentrant phases as a phenomenon

The 1975 phase diagram (Figure 1) was greeted with reserve for several years. As we will see in Section III, this is a common reaction to reentrant transitions.

In 1977, working in Bill Daniels' high pressure laboratory, we observed the reentrant behavior as a function of pressure even in pure compounds.[5,31] Furthermore, we found that the maximum pressure a smectic A_D phase supported was a sensitive function of the number of methylene groups interacting in the smectic layers. In the frustration picture, presumably, the fewer the number of methylene groups, the less deep the potential minima associated with the notches and the more susceptible the system is to permeation.

Pressure makes it harder to find the permeation minima that stabilize the layers. More frustrated triplets result and more dimers form. This is consistent with the monomer–dimer molecular picture. More dimers are formed with increasing pressure resulting in frustration of smectic order by the free permeation of monomers between layers. The smaller the background population of dimers at ambient pressures, the greater the pressure required to destabilize layers.

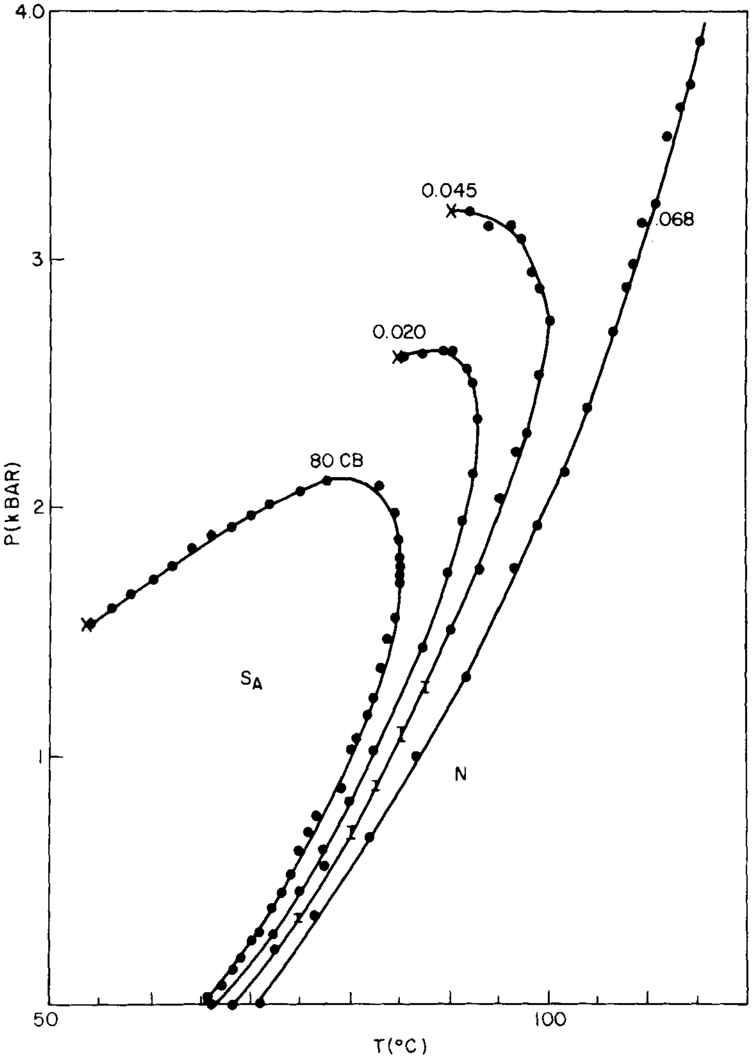


(a)

FIGURE 4 This figure shows the pressure temperature phase diagram of the 8OCB/6OCB mixtures (a) and the 8OCB/4O.8 mixtures (b). The X's represent crystallization. The maximum pressure a smectic A_D phase supports is a sensitive function of the chain length (a). In b, the numbers represent concentration of 4O.8. The maximum pressure increases with increasing concentration of 4O.8. The 4O.8 molecules weaken the strength of dipolar interactions between the 8OCB molecules and reduces frustration. The maximum pressure a frustrated A phase supports decreases with increasing frustration. (P.E. Cladis, *Mol. Cryst. Liq. Cryst.*, **67**, 177 (1981).)

Here[5,31] we specifically showed a bilayer structure of the smectic A_D phase consisting of dimers formed by overlapping the aromatic moieties of two molecules that was different from bilayer structures previously proposed by Gray and Lydon.[23] Simultaneously and independently, Leadbetter et al.[32] gave a similar model.

Leadbetter studied three kinds of selectively deuterated samples using neutron diffraction. In one type of sample, only the alkyl chains



(b)

FIGURE 4 (*continued*)

(the tails) were deuterated. In another, only the aromatic parts of the molecule (the cores) were deuterated. In the third, the whole molecule was deuterated. He was able to distinguish from the different contrasts found in neutron diffraction for these three samples and a non-deuterated sample that the "antiferroelectric" packing with overlapped cores (i.e., Figures 2b and c) was the most likely in the case of 8OCB.

Again, owing to the complexity of the molecules, we remark here that this result must be considered as a specific result applied to this particular molecule. When other interactions dominate, the system may choose another association such as the head to head dimers of Guillon and Skoulios[28] or one of the associations of Gray and Lydon.[23] We can even propose a dimer for the three benzene ring compounds, that has not yet entered the literature, where only one benzene ring overlaps.

Assuming the smectic A phase was surrounded by a line of first order phase transitions, Klug and Whalley[33a] and Clark,[33b] were able to fit our pressure data[5,30] to ellipses, not parabolas. Pershan and Prost[22] fitted our data[5,31] to parabolas but their fit does not look as pretty as the fit to ellipses.[33a,b] The conclusion one may draw (at a risk) from this is that ellipses are the signature of first order transitions and parabolas of second order phase transitions.

More recently, Kalkura and collaborators[34] made the important observation that the major axis of the ellipses was always parallel to the nematic–isotropic transition line! The reader is referred to the Kalkura paper[34] for many such examples. Figure 5 shows an example

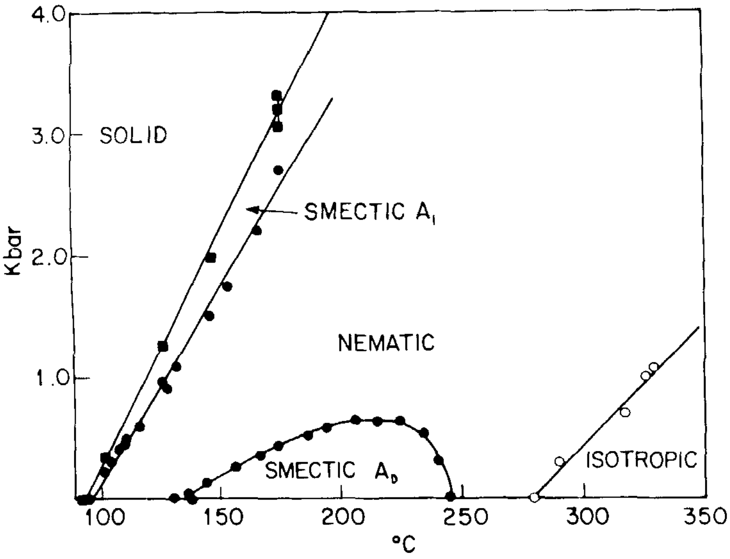


FIGURE 5 The pressure temperature phase diagram of an enclosed smectic phase (A_D) and an A_1 smectic phase. The compound is T8. (P.E. Cladis, in *Liquid Crystals*, S. Chandrasekhar, editor, Heyden publishers, Philadelphia (1980) p. 105.)

of an enclosed smectic A_D on a pressure–temperature phase diagram.[35] Kalkura et al.[34] pointed out that their observations were consistent with the existence of a coupling between the nematic and smectic A order parameters.[27,30,36]

Another of their important observations[34] is that the maximum pressure at which the smectic A_D phase was stable lay on a *universal* curve when plotted against the McMillan number, T_{NA}/T_{NI}: the ratio of the nematic to smectic A transition temperature to the nematic to isotropic transition temperature.[37] They generated two curves. Compounds with two benzene rings were on one curve and compounds with three benzene rings were on another curve.[34] These observations[34] suggest that the electronic structure of the benzene rings plays an important role in the formation of smectic A_D phases. Keyes has an, as yet, unpublished Landau theory[36] to account for these results by a coupling between the nematic and smectic A order parameter.

Shashidhar, Keyes and Daniels[38] also tested the optimum density model. They measured the volume of 8OCB (octyloxycyanobiphenyl) as a function of pressure. Their results did not support an optimum density model for the smectic A_D phase. This would not be surprising if the transition is weakly first order along the transition line.

Until 1979, the reentrant nematic phase was only observed in compounds with two benzene rings and in the super-cooled and the super-pressed[39] region of the phase diagram. In 1979, the reentrant nematic phase was discovered at one atmosphere, in pure compounds and in the stable region of phase diagrams.[40,41] The compounds were typically cyano compounds with three benzene rings.

It was interesting to read[42] that one of these compounds had been synthesized as early as 1976. However, the stable reentrant nematic phase it exhibited was identified as an unknown smectic phase,[43] or, as smectic B,[44] a more ordered smectic phase than smectic A_D. It was still more reasonable to postulate a more ordered smectic phase at a lower temperature than the smectic A phase even after the first report of the reentrant nematic phase.

In addition, the Bordeaux group[40] found compounds that exhibited a smectic A phase at a lower temperature than the reentrant nematic phase, the A_1 phase. We now think of the A_1 phase as involving correlations that include next nearest neighbor interactions (see Figure 2c and the discussion in the previous section). The layer spacing in this phase is close to the molecular length, so they called it smectic A_1. Later, several groups reported similar results on other compounds also with three benzene rings but with different linkages between the rings and different side groups.[45–48]

Since 1979, with great energy and ingenuity, the Bordeaux group succeeded in observing examples of multiple reentrance. These are phase transition sequences with decreasing temperature of nematic–smectic A_D–reentrant nematic–smectic A_D–reentrant nematic–smectic A_1. They also discovered the rich polymorphism of the simple smectic A phase.[49]

By examining the structure of molecules exhibiting the rich variety of short-range order in a single phase, one concludes that the aromatic cores, with different linkages is an important factor in determining reentrant behavior and smectic polymorphism.[50–52]

Gobl-Wunsch et al.[52] argue that reentrant phases in three- and two-ring polar compounds of cyano compounds were stabilized by similar molecular features. When the dipole of the links in the benzene system add to the cyano dipoles, reentrant phases dominate the phase diagram. This idea was elegantly demonstrated by Goodby.[51]

He synthesized two homologous series of compounds with only two benzene rings.[51] In one series, the ester dipole competed with the cyano dipole and, in the other, it supported the cyano dipole. Goodby et al.[51] found that this simple inversion of the COO linkage had a profound effect on the stability of the nematic phase relative to smectic phases. When the COO dipole enhances the cyano dipole, the nematic phase is preferred and reentrance occurs easily. When it competes, smectic phases are stabilized, and, in particular, the smectic C phase was observed.[51]

Similar observations were made by Tinh[50] for three ring compounds. His insight led him to synthesize the largest number of compounds showing reentrant nematic phases, including multiple reentrant nematic phases, and the large variety of smectic A phases discovered by the Bordeaux group.

Based on these ideas[50–52] and the high pressure results,[34] one speculates that sextuple and octuple reentrance predicted by Indekeu and Berker[18] may be obtained in polar compounds with four and five benzene rings and their mixtures.

D. Reentrant nematics and other smectic phases

In 1980, Weissflog et al.[53] found the reentrant nematic phase below a smectic C phase. Their phase transition sequence with decreasing temperature was: nematic–smectic A–smectic C–reentrant nematic. This same sequence was found by the Bordeaux group[54] and by Goodby et al.[51] in mixtures. In 1981, Pelzl et al. discovered another variation: nematic–smectic A–smectic C–reentrant nematic–smectic C[55] as well as other smectic phases, such as smectic B and smectic E, below the reentrant nematic phase.[45] From the molecular model shown in Figure 2c, a smectic C-like ordering provides relief for the unfavorable packing of overlapped dimers.

Shashidhar et al.[56,57] studied the reentrant nematic–smectic C–smectic A multicritical point as a function of pressure and in mixtures. They found that when this multicritical point was studied in mixtures closer to the nematic–isotropic phase transition temperature, the phase diagram showed the same universal topology[57] as the nematic-A–C multicritical point.[58]

E. Reentrant nematic in non-polar materials

Just after Tinh, Malthete and Destrade[59] discovered reentrant nematic phases in non-polar discotic liquid crystals, Pelzl et al.[60] found reentrant behavior in non-polar compounds as predicted to occur by Longa and de Jeu[61] and independently, using a steric packing argument, by Dowell.[62] It is clear that the dipolar interactions of the frustration theory do not apply to these compounds. Dowell's theory may be particularly useful for accounting for reentrance in non-polar rod-like and disc-like compounds. Longa and de Jeu's argument is also steric but different from Dowell's. Their mechanism is based on the unfavorable packing of paired molecules in layers (see for example, Figure 2) that becomes more unfavorable as the density within a layer increases.

F. Physical properties of the reentrant nematic phase in polar compounds

Using ESR, Luckhurst et al.[63] measured the orientational order of the reentrant nematic phase of the CBOOA/HBAB system. They used two kinds of spin probes: one sensitive to the orientational order of the aromatic moiety and one sensitive to the orientational order of the alkyl chain moiety. They found the orientational order to be continuous at the nematic–smectic A transition and the reentrant nematic–smectic A transition. In contrast, they observed a discontinuity in the gradient of the order parameter at the reentrant nematic–smectic A transition but not at the nematic–smectic A transition. Luckhurst and Timimi[64] accounted for this result by extending McMillan's mean field theory of the smectic A phase.[37]

By studying the NMR spectra on deuterated samples of 8OCB/6OCB mixtures, Vaz et al.[65] also observed continuity of the order parameter across the smectic transitions to both nematic phases.

However, they interpreted their results in terms of the coupled order parameter theory.[27,35,36]

Using proton NMR on the 8OCB/6OCB mixtures, Dong[66] also observed the discontinuity in the gradient of the order parameter at the smectic transition to the reentrant nematic phase but not to the high temperature nematic phase. He pointed out that this difference meant that the molecular dynamics were not identical in the two nematic phases. This difference is reflected in the high frequency limit of some transport properties and only subtly in the static or low frequency limit.

For example, a slight asymmetry is observed in the twist viscosity, γ_1 in smectic A_D.[67] Bhattacharya and Letcher[68] had measured the Miesowicz viscosities[69] in both nematic phases and found no anomaly in either η_a (the director is perpendicular to the plain of shear) or η_b (the director is in the plane of shear parallel to the velocity), and only a small anomaly for η_c (the director is in the plane of shear and perpendicular to the velocity).[68]

Static and low frequency conductivity measurements find no difference in the electrical conductivity of the two nematic phases. On the other hand, measurements in the kHz range show a dramatic pretransitional effect in the smectic A phase as the reentrant nematic phase is approached.[70] The conductivity was measured parallel ($\sigma_\parallel$) and perpendicular ($\sigma_\perp$) to the optic axis. As the reentrant nematic phase is approached, $\sigma_\parallel/\sigma_\perp$ increases dramatically. This result is compatible with nearly free permeation perpendicular to the layers of frustrated monomers with the formation of dimers at the transition to the reentrant nematic phase.

Another result compatible with frustration theory is the observation of two incommensurate lengths in the reentrant nematic phase[71,72] but only one in the high temperature nematic phase. Guillon et al.[39] observed two lengths in the high pressure reentrant nematic phase of CBOOA as well as in mixtures with HBAB. The interpretation was microcrystallites coexisting with the reentrant nematic phase. In the light of these later measurements[71,72] and a frustration model, the data of Guillon et al.[39] may be reinterpreted as the coexistence of two different smectic fluctuations similar to the one given by Nishihata et al.[71] and Fontes et al.[72] These authors[71,72] were studying a three ring compound that exhibited a stable smectic A_1 phase below the reentrant nematic phase. In the Guillon case,[39] the lower temperature smectic phase would have to be a tilted phase, probably smectic C (see Figure 6).

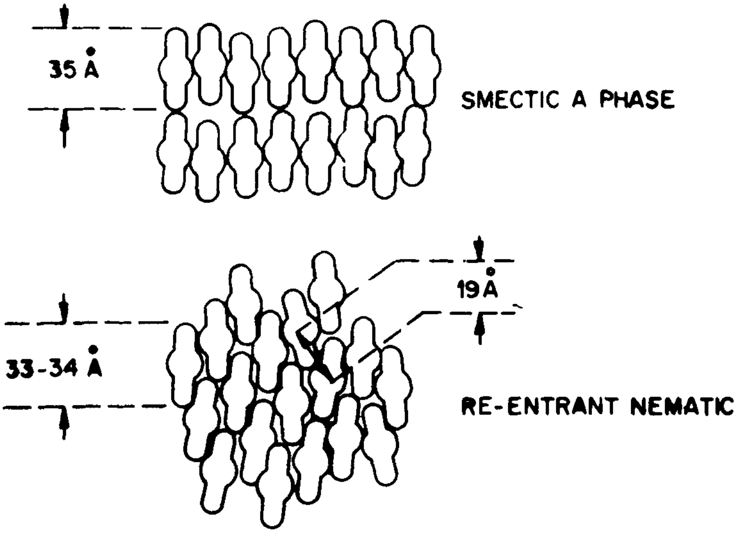


FIGURE 6 The possible smectic C short range order associated with correlated triplets perhaps responsible for the reentrant nematic phase in the supercooled mixtures of CBOOA and HBAB. (D. Guillon, P. E. Cladis and J. Stamatoff, *Phys. Rev. Lett.*, **41**, 1598 (1978).)

Kortan et al.[73] did not observe the coexistence of lengths in the supercooled mixtures of 8OCB/6OCB. Nor did they observe evidence for the overlapped dimers that were postulated to destabilize the smectic A_D phase.[61,74] But this result may be compatible with a statistical notion of dimers as correlated pairs rather than a static one. They found that the degree of in-plane order was not related to the smectic order parallel to the layers. This suggests that the approximation of ignoring the degree of in-plane order adequately describes smectic ordering parallel to the layers.[18]

In their 1988 paper,[18] Indekeu and Berker find no change in the dimer concentration across the reentrant nematic–smectic A_D transition line. They argue that this result agrees with the dielectric measurements of Ratna et al.[75] In contrast, the mean field model[61] predicts an observable change in dimer concentration across the smectic A reentrant phase transition. We note that the index of refraction measurements of Chen et al.[76] seem more similar to the estimate Chandrasekhar[77] made of dimer concentration from the mean field theory of Longa and de Jeu.[61]

Garland and coworkers[78] did not observe a heat capacity anomaly at the nematic–smectic A or reentrant nematic–smectic A transition of the 6OCB–8OCB mixtures even though they visually observed that the transition existed. They obtained a similar result when studying the reentrant phase of pure 8OCB as a function of pressure.[79]

Differential thermal analysis carried out on several three ring compounds (one called T8, octyloxybenzoyloxy cyano stilbene) with stable reentrant nematic phases and a low temperature smectic A_1 phase found a strong temperature dependence of heat capacity in the reentrant nematic phase and a significantly smaller thermal anomaly at the reentrant nematic–smectic A_D transition.[80] These authors interpreted their results as supporting the phenomenological optimum density model.[22] On the other hand, Indekeu et al.[81] working on T8 using high resolution ac calorimetry, found the nematic and reentrant nematic to smectic A_D transition enthalpies to be comparable. However, a significantly larger excess heat capacity was observed at the reentrant nematic–smectic A_1 transition. They found their result to be consistent with the increase in correlations expected in the A_1 phase as dimers and monomers condense to the ordered triplet state.[81]

High resolution x-ray scattering measurements of 8OCB and 6OCB mixtures by Kortan et al.[73] found identical pretransitional smectic A behavior in both the nematic and reentrant nematic phases. These results were recently verified by Ivanov et al.[82] with nearly identical results. Both groups were fitting their data to the functional form predicted by the optimum density theory.[22]

Dynamical light scattering experiments of Miyakawa et al.[83] found exponents compatible with mean field but not with dynamic scaling at the reentrant nematic to smectic A phase transition. They were studying a three ring compound, NBCA (nonyloxy-benzoyloxy cyano azobenzene) that has a stable reentrant nematic phase. In addition, they observed no difference in the exponents for bend and twist. These authors were fitting their data to the usual simple functional form.

Using the technique of heterodyne photon-correlation spectroscopy, Fromm[84] studied twist and bend modes in 8OCB/6OCB mixtures. He found that his data agreed with the Jahnig and Brochard theory[85] provided he assumed cross-over from an anisotropic to an isotropic critical regime as the nematic–smectic A transition temperature is approached. No difference was found in the exponents for bend and twist[84] agreeing with the result of Miyakawa et al.[83]

Fisch et al.[86] found that the layer compressibility, B, in 8OCB–6OCB mixtures to be discontinuous at the high temperature nematic–

smectic A transition. They interpreted this result to mean that either the transition was first order, or an entropy-driven Kosterlitz-Thouless phase transition, postulated by Nelson and Toner in a private communication to Fisch et al.[83]

G. Some remarks

As is normal when our intellectual framework has been shaken by counter-intuitive observations, such as the reentrant nematic, new ideas are generated, each with a germ of truth and each in its own way successful on some scale in describing the obervations. The Pershan-Prost optimum density idea[22] is a simple but global way to think of reentrant transitions. It may still be useful to describe multiple reentrance by coupling it, for example, to the changing microscopic structure that emerges from a statistical description of Berker et al.[17-19] that includes steric contributions. It is the only existing model that has made predictions about the nature of the reentrant phase transition line.[22]

Although the frustration model is a closed form solution of the partition function using a map (the prefacing transformation) similar to the renormalization group map,[17-19] it introduces singularities on the transition line. Thus, no predictions may be deduced from it about critical exponents or other features of the transition.

Another feature of the frustration model is the construction of discrete positions, identified with notches in the alkyl chain, used to evaluate the phase diagrams. The pressure data showing universality depending only on the number of benzene rings,[34] suggest that chains may not be the most important molecular parameter determining reentrance. Another suggestion is to identify these notches with the aromatic moiety instead of the chains.

Mean field theories[28,61,64] are also useful but fluctuations need to be incorporated. Owing to the short range nature of the intermolecular forces and the delocalization of the molecules in the liquid state, a statistical description is required to extend our understanding to the molecular dynamics and short range forces that lead to reentrance. The Prost and Barois theory[24] is another attractive description of the physics of reentrance but a microscopic argument is needed to justify the selection of the two lengths in their theory. With some interpretation, the frustration theory seems to do this. For example, their A_1 model[24] can just as easily be replaced by the Berker et al. condensate of triplets.[18,19]

Even though we have bowed to former usage in this article, it seems more appropriate to call the completely interdigitated, unfrustrated phase smectic A_I rather than smectic A_1 where I stands for interdigitated. The existence of this phase has recently been confirmed to exist in lipids.[87] In this way it will be clear that the A_I phase has a different structure from the non-polar monomer packing of A. Owing to its large density and unfrustrated structure stabilized by next nearest neighbor interactions, it seems unlikely that this A_1 phase will be destabilized by either an A_D phase or the nematic phase or the A_1 phase with only nearest neighbor interactions.

Even the non-rigorous coupled order parameter model of experimentalists[27,30,36] successfully describes the pressure temperature phase behavior of reentrant nematics. It is interesting to note that this appears as a feature of Hida's[88] two-dimensional lattice model but not of the early frustration model[17] nor the more recent 2-d model of Walker and Mace.[89] Hida takes into account specific molecular interactions that are compatible with the molecular picture (Figure 2c). In the frustration theory, although the coupling constants turn out to be highly temperature dependent, the orientational order is assumed to be perfect at all temperatures.

III. HISTORY AND THEORIES OF REENTRANT PHASE TRANSITIONS

A. Rochelle salt

Rochelle salt (sodium potassium tartrate tetrahydrate, $NaK{\cdot}T{\cdot}4H_2O$) was first prepared in 1655 by Seignette in La Rochelle, France.[90] Rochelle salt is chiral, *dextro*, when synthesized from tartaric acid obtained from the grape industry. For a long time it was valued for its medicinal properties. Then, in 1880, the Curie brothers discovered its piezoelectric properties extending its use to a number of important, technical applications especially in acoustics.

As mentioned in the introduction, in 1921, Valasek[3] discovered that Rochelle salt exhibited a spontaneous polarization in the temperature interval 24°C and −18°C. This makes Rochelle salt the oldest, and for a long time after its discovery it was the only ferroelectric crystal known. The unique feature of the ferroelectric property in Rochelle salt is that it has two Curie temperatures, an upper and a lower one. It may well be the first known case of a reentrant transition.[3]

The ferroelectric phase in Rochelle salt is associated with a monoclinic crystal structure. Above and below this temperature interval, the crystal structure has a center of symmetry (i.e., is orthorhombic) and there is no spontaneous polarization but it is piezoelectric. According to Jona and Shirane,[91] the two orthorhombic phases are identical but the structure is not known with much precision in the monoclinic phase. According to Kanzig,[15] the low temperature paraelectric phase is not antiferroelectric.

Phase diagrams of solid solutions of Rochelle salt with its isomorphous tartrate, sodium ammonium tartrate $\cdot 4H_2O$ are particularly fascinating. Figure 7 is from the thesis of Melmed.[92] Attention is drawn to the small reentrant ferroelectric region in the concentration range between zero and 2.4% $NaNH_4{\cdot}T{\cdot}4H_2O$. This part of the phase diagram was first reported in 1936 by Kurchatov.[93] A more complete phase diagram was eventually published in 1958 by Makita and Takagi.[94]

In this concentration range, increasing amounts of the sodium ammonium double tartrate brings the two Curie temperatures closer together. The ferroelectric phase ceases to exist in the concentration

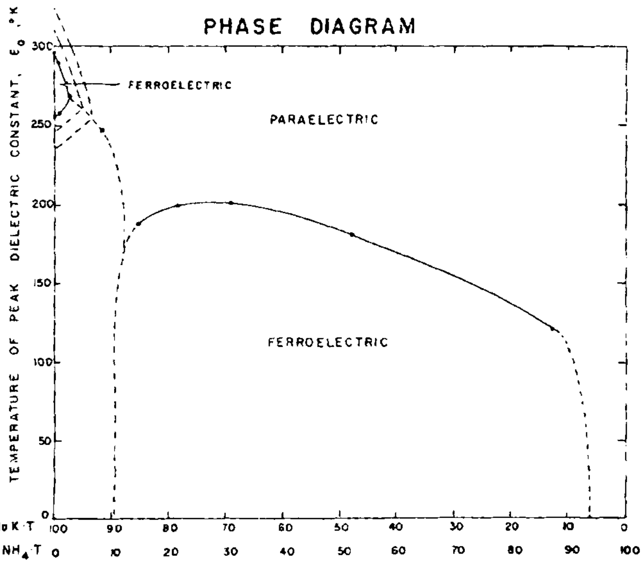


FIGURE 7 The phase diagram of Rochelle salt mixtures with sodium tartrate. This phase diagram is from the unpublished Master's thesis of A. J. Melmed at Pennsylvania State University. The reentrant part was first reported by I. V. Kurchatov in *Le champ moleculaire dans les dielectriques* (*le sel de Seignette*), Hermann, Paris (1936). The dotted line joining the two ferroelectric regions of the phase diagrams may not be a phase transition line. On the other hand, it may be a paraelectric–spin glass transition line.

range 2.5 mole% to 10 mole% $NaNH_4 \cdot T$. A new ferroelectric phase with a single Curie point shows up at much lower temperatures, when the concentration of NH_4Na double tartrate exceeds 11 mole percent.[92-94]

The dotted line in the paraelectric region between these two concentration limits, traces a temperature anomaly in the dielectric measurements. This anomaly means that the upper and lower non-polar phases of Rochelle salt are, possibly, not quite isostructural.[91] Another possibility is that it is a paraelectric–spin glass transition line due to frustration of the water dipoles in the monoclinic lattice. If the low temperature paraelectric phase is not a spin glass, then the phase diagram of Rochelle salt in the relevant, for this article, low concentration range may well be the first example of a reentrant phase diagram like Figure 1 ever observed in physics.

Owing to its lyotropic features, not its ferroelectric properties, the reentrant transition of Rochelle salt may share similarities with the uniaxial–biaxial–uniaxial transitions discovered by Saupe in lyotropic nematic systems.[95] This transition has recently been discussed in terms of a mixture of rods and discs.[96] As is well known, the symmetry of nematic (uniaxial and biaxial) and cholesteric phases exclude them from being ferroelectric. Thus, we stress, the Rochelle salt phase diagram is unrelated to reentrant cholesteric phases.[97-99]

It may, however, share certain similarities with smectic X, a truly ferroelectric liquid crystal discovered by Brand and Cladis.[100] For example, a compound may exist that shows the sequence of phase transitions with decreasing temperature: helielectric or orthogonal smectic, smectic X, orthogonal smectic. The two orthogonal smectics may even be the same. The helielectric phase does not exhibit a polarization in the absence of a field and rotational symetry in the plane of the layers, excludes orthogonal smectic phases, such as A and B, from exhibiting a spontaneous polarization. Since smectic C* is not observed to be piezoelectric, the physics of the Rochelle salt transitions is probably not related to the reentrant distorted smectic C* phase observed by Kondo et al.[101] in an electric field.

B. Nicotine and water

A reentrant behavior that has been known for some time, but not usually called so until recently,[102,103] occurs in some mixtures, such as nicotine and water. As a function of temperature, T, and concentration, x, nicotine and water mix everywhere in the (x, T) plane except in a closed region where they are immiscible. At a particular concentration that crosses the enclosed two phase region, with increasing temperature, the two components are miscible, then phase separate, then are miscible again. The stability of mixtures is described by a chemical potential and instability to diffusion controls this example of reentrant behavior.

Phase separation is not observed at the reentrant transition discussed in the previous sections. On the other hand, this kind of an argument may be relevant to describe the miscibility gap in some mixtures.[29,30]

Most recently, Sigaud et al.[104] have extended the reentrant nematic phenomena to include mixtures of small molecular weight liquid crystals with polymeric liquid crystals. Because of the large difference between these two components, they point out that phase separation may indeed be a feature of the reentrant behavior of this system.[105,106]

C. Magnetic superconductors

Another example of reentrant behavior is the superconducting normal metal transition first observed[107] in 1971 following the predictions of Muller-Hartmann and Zittartz.[108] The superconducting state is stabilized by correlated electron pairs called Cooper pairs. The spins of the Cooper pairs are anti-parallel. In the Kondo effect, an anti-ferromagnetic exchange interaction flips the electron spins when they are scattered by magnetic impurities. These authors[108] predicted that the Kondo effect would lead to a weakening and eventual destruction of superconductivity at very low temperatures. At temperatures much below the Kondo temperature, they also predicted that superconductivity could reappear just as the smectic A phase reappears below the reentrant nematic phase.

When the impurity atoms are few and statistically distributed in the host, the two normal metal phases could be identical. If the normal and the reentrant normal states are identical, then this phase transition would be a close analogue to the reentrant nematic. It was proposed to call these kinds of superconductors, Kondo superconductors.[109]

These results[107,109] were considered controversial and probably a result of sample inhomogeneities. The reentrant phenomenon in superconductors was not completely accepted until the discovery of magnetic superconductors in 1977.[2,110] It is ironical to realize that this was because magnetic superconductors are not truly reentrant and, therefore, easier to understand. In contrast, the remarkable feature of the reentrant nematic (and perhaps some of the Kondo superconductors) is that the two nematic phases appear to be identical for all parameters in the long time and long wavelength limit. The reentrant normal metal state in magnetic superconductors is associated with the onset of long range magnetic order. Here, the two normal metal states are not identical: one is magnetic and the other is not. A tour around the ordered smectic phase crosses a phase transition line. It is interesting that this difference has been recognized by library cataloguing systems. When referring to superconductivity the term reentrance is now to be replaced by "magnetic superconductors."

At low enough temperatures, inorganic materials tend to be either magnetic or superconducting.[111] As a function of decreasing temperature, some rare earth compounds first become superconducting, then magnetic. The return to the normal metal state coincides with the onset of long range magnetic order. The zero resistance state will be reentrant but on going around this state from the low temperature normal metal to the high temperature normal metal, a magnetic phase transition line intervenes.

D. Reentrant spin glass

A similar possibility exists for the paramagnetic, ferromagnetic, spin-glass system in three dimensions. Again, as a function of decreasing temperature, the phase sequence, paramagnetic, ferromagnetic and spin glass is observed. A plot of the magnetization as a function of temperature shows the magnetization first growing, reaching a maximum then decreasing to zero at the transition to the ferromagnetic–spin glass transition. But a tour around the ordered ferromagnetic state crosses a paramagnetic–spin glass transition line.[112]

E. Reentrant transitions in two dimensions

1. Magnetism on 2-d lattices. In 1965, Vaks, Larkin and Ovchinnikov[14] gave the first theoretical demonstration of reentrant behavior by studying Ising spins on a centered square lattice. They considered a competition between nearest neighbor (along diagonal directions) and next nearest neighbors (along horizontal and vertical directions). For an extremely narrow range of interaction strengths, they found reentrance.

In 1986, Morita[113] studied the Ising model on a "Union Jack" lattice. The "Union Jack" lattice is a centered square lattice with different horizontal and vertical interactions as well as two kinds of "diagonal" interactions. Morita found that reentrance occurred because the effective nearest neighbor interactions exactly canceled the next nearest neighbor contributions for particular values of the interaction constants. Again, reentrance is only expected for a tiny range of coupling constants. It is interesting to note that Berker et al.[17-19] observe a similar canceling of interactions in their theory.

A recent amusing lattice showing reentrant behavior in 2-dimensions is the Kagome lattice.[114] In this lattice, spins are placed at the corners of a rectangular lattice. Another spin is placed in the center of every other rectangle in both directions. These authors point out that an essential feature to obtain reentrance is frustration.[114] In their frustrated state (they call it *X*), the spins on the corners are ordered but the spins at the center of the rectangles are frustrated. The free energy of the completely ordered state (they call it *F*) and the frustrated *X* phase are equal only at $T = 0$. It is the greater entropy of the frustrated state that lowers its total energy relative to the ordered state with increasing temperatures. But a disordered phase always intervenes between the ordered and frustrated phase when the transition is second order.

In two dimensions, Huse et al.[115] generated several reentrant phase diagrams using a mock ANNNI (axial next nearest neighbor Ising) model. They made the important observation that reentrance did not survive in three dimensions because the entropy term in three dimensions does not become large enough to overcome the free energy as it does in two dimensions. It is difficult, but not impossible,[10,25] to frustrate a system on a lattice in three dimensions.

Even in two dimensions, quenched random nearest neighbor interactions on a lattice do not lead to frustration and reentrance does not occur.[116] This poses a question about reentrant theories of liquid crystals based on 2-d models on square lattices.[88,89] Will they survive in the three dimensional world of liquid crystals? The Berker et al.[17-19] theory ingeniously escapes into the third dimension with their system of notches. Their spins are perpendicular to the 2-d layers of the smectic. In the Ising lattice, the spins are in the plane of the lattice.

In two dimensions, the spin glass–paramagnetic transition occurs at $T = 0°K$. In one of his last papers, McMillan showed[117] using a renormalization group strategy that the ferromagnetic–paramagnetic transition, when only nearest neighbor interactions were considered, could possibly be reentrant when $T/T_c < .5$. He found $T = .5T_c$ was a bicritical point on the ferromagnetic–paramagnetic critical surface that divided the critical surface into two portions. When $T > T_c$, the critical behavior is controlled by the pure Ising fixed point whereas for $T < T_c$, it is controlled by the ferromagnetic–spin glass fixed point. In McMillan's model, the bicritical point does not coincide with the triple point.

For example, on the Kagome lattice,[114] the bicritical point is at T = 0 and the triple point coincides with it. A disorder line separates the two critical regimes. Fluctuations on one side of the disorder line carry the system to the frustrated X phase and on the other side, to the ordered F phase.

2. *Krypton on graphite.* In these experiments,[7] krypton atoms are spread onto the surface of graphite. At low coverage the state of krypton is fluid as they are not localized at a particular graphite site. With increasing coverage, the fluid (F) phase condenses to the ordered commensurate (C) phase (a 2-d solid) that, in its turn, melts to a reentrant fluid phase (RF) at higher coverage. Eventually, the RF phase transforms to an incommensurate solid phase (IC).

While the C–F transition was immediately recognized as a melting transition, the C–RF transition was initially characterized as a transition from commensurate to incommensurate solid. However, the first synchrotron x-ray study[7] of this system in 1981 showed that at least above 80°K, a disordered phase existed between the two solid phases. It is possible that this work was stimulated by the earlier work of Moncton and Birgeneau with Guillon and Cladis[118] at Bell Laboratories of the structure factor in the reentrant nematic phase transition.

These experimental results[7] stimulated theorists to rethink the problem of the commensurate–incommensurate solid phase transition. It would lead to the realization that a liquid (disordered) phase would always intervene for a set of interactions specific to this system, between the two states.[119,120] The phase diagram these authors calculate does not show reentrance, but the ingredients are there as subsequently shown by Kaflisch et al.[120] The IC phase is an example of a frustrated state and has been called a "floating phase."[120]

F. Spin gas model for multiple reentrant phase transitions

Simultaneously with the development of the ideas generated to understand the commensurate–reentrant fluid[119,120] transitions, Berker and collaborators[17–19] formulated a spin-gas model to explain reentrant behavior in liquid crystals. It shares many similarities with the theories mentioned above. The interest in this theory is that it shows how frustration can lead to reentrance in three dimensions.

Their model seeks to explain the observed single reentrance (N–A_D–N), double reentrance (N–A_D–N–A_1), "quadruple reentrance" ($N-A_D-N-A_D-N-A_1$) in polar compounds. The theory also predicts reentrance below A_1 in polar compounds as well as sextuple and octuple reentrant behavior.[18-19]

The key feature of their model, similar to all models of reentrance, is *frustration* resulting in near cancellation of forces between molecules with strongly dipolar heads and their neighbors, in the close packing of a liquid. In analogy to phase transitions in 2-dimensions, the A_D phase (and their A_1 phase) is a frustrated phase similar to the floating phase of krypton on graphite[119,120] and the X phase of the Kagome lattice.[114] In this analogy the nematic phase is a disordered phase.

Usually, a second order transition, where fluctuations dominate, cannot occur directly from an ordered state to the frustrated state. A disordered phase intervenes. A first order phase transition can always occur between these two states but as the phase transition becomes more second order the likelihood of an intervening disordered state, due to fluctuations, becomes greater.

It has been proposed that this scenario has been observed experimentally[121] along a first order smectic A_D-A_I transition line approaching a critical point. Before the critical point could be reached, a nematic island occurred. On the phase diagram, the island is embedded in the smectic A_D phase. This embedding shows that while the A_D phase is frustrated, the A_I phase is not. Prost and Toner[122] have formalized some of these ideas in a defect theory of the nematic–smectic A phase.

The mechanism of nematic reentrance is frustration of dipoles resulting from competing antiferroelectric (associated with smectic A_D) and ferroelectric (that they associate with smectic A_1 or A_2) interactions. When frustration is relieved by permeation on atomic and smaller (oscillations in the potential wells that they term libration) length scales, smectic reentrance results. Correlated dipoles that are, loosely speaking, similar to dimers, frustrate smectic order and favor the nematic phase. Calculated dimer concentrations are insensitive to $N-A_D$ transitions, however a large enthalpy is expected at the $N-A_1$ condensation of correlated triplets, as indeed observed.[81]

IV. CONCLUSIONS

It has not been possible to reference all the remarkable work that has been devoted to studying reentrant transitions in liquid crystals. In particular, I have not mentioned the interest in the reentrant nematic phase for improving the contrast of devices because of their enhanced orientational order.[123]

Reentrant transitions pose a difficult many body problem. It is not surprising, therefore, that our knowledge is considerably broader than it is deep. We have seen that it is not easy to obtain reentrance from any theory. And when it is found, in, for example, frustrated systems in two dimensions, it only occurs for a small range of coupling constants and disappears entirely in three dimensions.[115] The success of the Berker et al. theory[17–19] is indeed remarkable in this respect. Not only does it describe simple reentrance in three dimensions, it also predicts multiple reentrance. Furthermore, it is possible to relate the structure of the various frustrated and unfrustrated phases to intuitively acceptable molecular associations.

In the next one hundred years of liquid crystal research, we look forward to the development of these ingenious therories and experiments to deepen our understanding of what was once an isolated curiosity and is now an established phenomenon: reentrant phase transitions. In a general sense, they have changed the way we think about phase transitions.

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