6-15-1977

Nematic-Smectic-A-Smectic-C Polycritical Point - Experimental-Evidence and a Landau Theory

David Johnson
Kent State University - Kent Campus

David W. Allender
Kent State University - Kent Campus, dallende@kent.edu

Richard deHoff
Kent State University - Kent Campus

Craig Maze

Everett Oppenheim

See next page for additional authors

Follow this and additional works at: http://digitalcommons.kent.edu/phypubs
Part of the Physics Commons

Recommended Citation

This Article is brought to you for free and open access by the Department of Physics at Digital Commons @ Kent State University Libraries. It has been accepted for inclusion in Physics Publications by an authorized administrator of Digital Commons @ Kent State University Libraries. For more information, please contact earicha1@kent.edu, tk@kent.edu.
Nematic–smectic-A–smectic-C polycritical point: Experimental evidence and a Landau theory

David Johnson,* David Allender, and Richard deHoff

Department of Physics, and Liquid Crystal Institute, Kent State University, Kent, Ohio 44240

Craig Maze, Everett Oppenheim, and Reese Reynolds

Motorola Incorporated, Phoenix, Arizona 85008

(Received 28 July 1976; revised manuscript received 26 October 1976)

Differential-scanning-calorimetry measurements and optical-microscopy observations are reported on mixtures of two stable liquid crystalline compounds, one of which has the nematic, smectic-A and smectic-C phases, while the other has only nematic and smectic C. The phase diagram for this system is found to have the following features: (i) a line of second-order nematic–smectic-A transitions with large pretransitional effects, (ii) a line of continuous smectic-A–smectic-C transitions, (iii) a line of first-order nematic–smectic-C transitions with very weak pretransitional effects, and (iv) a multicritical point where these three lines meet. A phenomenological Landau-like theory is presented, which qualitatively describes the observed phase diagram. On the basis of this work it is argued that the nematic–smectic-C transition is always of first order.

I. INTRODUCTION

Recent interest in the study of higher-order critical points,1 called poly- or multicritical points, has led to the discovery of apparent tricritical2–4 behavior in several liquid-crystal systems. As of now, only the nematic (or cholesteric) to smectic-A phase transition has been studied in this manner. It has been found that these transitions may apparently be changed from first to second order by application of pressure2,3 or by mixing.4 The binary-mixture study was first suggested by Alben5 who has more recently suggested6 that one might find a higher-order critical point in a binary-mixture system where one component has nematic (N), smectic-A (A), and smectic-C (C) phases and the other has only N and C phases. Mixing such compounds would result in a phase diagram exhibiting an A phase that gets squeezed out. This would happen at a polycritical point if at that point the three phases become the same, or at an ordinary triple point if at that point the three phases coexist.

We have found such a binary-mixture system7 that exhibits a polycritical point. The phase diagram is shown in Fig. 1, and the polycritical point (PCP) has some unusual features which we report and discuss here.

II. EXPERIMENT

The phase diagram of Fig. 1 was determined in two independent ways, namely, differential scanning calorimetry (DSC-2)8 and thermal microscopy. The latter was also used to characterize the phases. Transition temperatures determined by these two methods agreed to within 0.5 °C; except for the AC transitions which, because they produced only a slight change in slope on the DSC-2 traces could only be determined by this method to within ±2–3 °C. Thermal microscopy on homeotropically aligned samples, on the other hand, allowed us to determine the AC transition temperatures to within ±0.1 °C. The most striking features of the DSC-2 data are as follows: (i) the AC transitions are continuous and show little or no pretransitional effects; (ii) the NA transitions are continuous and show rather strong pretransitional effects which vanish as the PCP is approached [see Fig. 2(b)]; (iii) the NC transitions are very weakly first order and show very weak pretransitional effects [see Fig. 2(a)]. The NC latent heats vanish as the PCP is approached, as shown in Fig. 1.

The near absence of NC pretransitional effects is especially striking when placed in perspective with the present and previous4 work on the NA transition. The NC latent heats are extremely small, the largest being only ~0.1Rm, and the smallest detected one ~0.01Rm, where Rm is the ideal gas constant. NA transitions having such small latent heats exhibit very pronounced pretransitional anomalies,4 whereas these extremely weak NC transitions are by comparison void of pretransitional effects. We discuss pretransitional effects briefly later, but we have no clear explanation for these differences. The most pronounced feature of the DSC-2 results is that the PCP in Fig. 1 is a point where a line of weak and decreasing first-order NC transitions branches into two lines of continuous transitions, namely NA and AC transitions.

Our microscope studies of the NC transition reveal that the tilt angle just below the NC transition is finite and decreases monotonically to zero.
as the PCP is approached. This fact indicates that there is a discontinuity in the optical property of biaxiality which complements the latent heat data by suggesting that the NC transition is first order. On the other hand, the AC transitions are continuous as determined by both conoscopic and orthoscopic observations. We proceed to discuss these results.

III. DISCUSSION

It has been shown by de Gennes\(^{9}\) that the NA, AC, and NC transitions may all be continuous according to the Landau rules.\(^{10}\) Therefore, one expects to have the possibility here of finding an NAC polycritical point where three lines of continuous transitions meet, i.e., the NA, AC, and NC lines. Since the NC line is a line of first-order transitions the point in Fig. 1 where the three lines meet is not this kind of a point; therefore it is somewhat unexpected and consequently interesting. The fact that the NC line branches at the polycritical point into the NA and AC lines, both of which are lines of continuous transitions, suggests that this may be a bicritical point. However, as we will show, using existing Landau theories, this is not the case. This point is a new kind of polycritical point having neither tricritical,\(^{11}\) tetracritical,\(^{12,13}\) nor bicritical\(^{12,13}\) characteristics. In fact, Chen and Lubensky\(^{14}\) have recently suggested that it is a Lifshitz point.

Phenomenologically bi- and tetracritical behaviors are thought to occur as a result of competition between two kinds of order expressed in Landau theory by the free-energy expression

\[
F = \alpha \psi^2 + \frac{1}{2} \beta \psi^4 + a_1 \eta^2 + \frac{1}{2} b \eta^4 + c \eta^2 \psi^2,
\]

where \(\eta\) and \(\psi\) are the order parameters and \(\alpha = \alpha_0 (T - T_c)\), \(a = a_0 (T - T_c)\), and \(\alpha_0\), \(a_0\), \(b\) > 0. The coupling coefficient \(c\) may be positive or negative, but if \(c < 0\), then we must have \(c^2 < \beta b\).

One phase diagram for such a free energy is illustrated in Fig. 3(a). There we see that for \(c^2 < \beta b\) four phases are allowed, namely, I (\(\psi = \eta = 0\)), II (\(\psi \neq 0, \eta = 0\)), III (\(\psi = 0, \eta \neq 0\)), and IV (\(\psi \neq 0, \eta \neq 0\)) and all of the phase transitions are continuous, and meet at the so-called tetracritical\(^{12,13}\) point. If, on the other hand, \(c^2 > \beta b\) the most ordered phase (IV) gets squeezed out and the
transition line between the ordered phases (II and III) becomes a first-order line whereas the two disordered to ordered phase transitions (I- II and I-III) remain continuous. Figure 3(b) shows a typical phase diagram for this type of behavior which has been designated as bicritical. The first-order antiferromagnetic to spin-flop transition and superfluid to solid transition in He$^4$ are thought to epitomize such behavior at the point where they branch into second-order lines of transitions into the disordered phases.

For the purpose of attempting to understand the present case of an NAC polycritical point on this basis, we assign to $\psi$ the role of the amplitude of the density wave normal to the smectic layers and to $\eta$ the role of some measure of biaxial order. Thus the tetracritical phase diagram would then have the following phases: (I) Uniaxial nematic $\eta = 0$; (II) smectic A (uniaxial smectic) $\eta = 0, \psi \neq 0$; (III) biaxial nematic $\eta \neq 0, \psi = 0$; (IV) smectic C (biaxial smectic) $\eta \neq 0, \psi \neq 0$; whereas the bicritical phase diagram would have a first-order biaxial nematic to smectic-A line branching into two second-order lines from uniaxial nematic to biaxial nematic and smectic A. Neither of these correctly describes the present situation where we have no biaxial nematic phase. That is, unlike the bicritical phase diagram, the most ordered phase (smectic C) is present in our phase diagram instead of the biaxial nematic.

We have attempted to reproduce the phase diagram by adding a term of order $\eta^2$ to Eq. (1) and letting $b$ vary as some linear function of $T_1 - T_2$. Both signs of the coupling coefficient $c$ were considered. It appears from these calculations that any expression that has terms involving $\eta$ alone and hence allows in principal for a biaxial nematic is unable to give the experimentally observed phase diagram. One can arbitrarily abolish the biaxial nematic phase by fixing $a > 0$ and allowing $c$ to vary. This also fails to give the correct phase diagram.

From the point of view of the present state of liquid-crystal physics there is nothing unusual in this. No convincing experimental data has been reported which supports the existence of a biaxial nematic phase, whereas the smectic-C phase is common and never occurs in temperatures above the smectic A which, in turn, seldom occurs above the nematic. So our experimentally observed phase diagram is, from that point of view, what one might expect. In fact, the order in which these phases occur and the absence of any biaxial nematic phases has led theoreticians to develop Landau theories in which biaxiality cannot occur in the absence of layers. This is reasonable because biaxiality appears to be intimately connected with and may just passively follow from tilt of the molecules relative to the layer normal. Therefore, since tilt cannot be defined in the absence of layers, free energies of the general form

$$F = \alpha \psi^2 + \frac{1}{2} \beta \psi^4 + \psi^2 (\alpha q^2 + \frac{1}{2} \beta q^4 + \gamma q^2 \psi^2)$$

in which $\eta$ never appears without $\psi$, have been suggested. The dependencies of the various
choice of coefficients, this expansion has been reported to result in a phase diagram generally like the experimentally observed one except that the NC transition line was calculated to be a line of continuous rather than first-order transitions.

One way to produce first-order transitions is to allow the coefficient $a$ in Eq. (2) to change sign at a critical concentration and add a term in $\psi$. An approach similar to this is the treatment of the tricritical point which has been observed to occur on the NA transition line in 80.3–20.3 mixtures. By including a term in the free energy of the form $-c(5S)\psi^5$, de Gennes has taken into account the coupling of the smectic order parameter to fluctuations in the degree of nematic order. The result is that the coefficient $\beta$ goes like a constant term supplemented by an additive term dependent on the distance in temperature from the NA transition from the isotropic-nematic transition: the narrower the nematic range, the smaller $\beta$ becomes.

However, in the case of 785–885 mixtures, the widening nematic range corresponds to increasing NC transition entropy, as is readily seen in Fig. 1. This is opposite to the behavior expected from coupling between smectic and nematic fluctuations. For this reason, we believe that fluctuations of the nematic order do not have a large role in determining the gross features of the phase diagram and consequently we shall neglect such effects in our description. In passing, it is worth noting that an appropriate mixture might have a tricritical point on the NA line so that, as a function of concentration, we would have a first-order line which turns into a second-order line which then merges with another second-order line (AC) forming a first-order line (NC). If, on the other hand, the nematic fluctuations are important in the sense of Halperin, Lubensky, and Ma then the NA line may always be very weakly first order and the PCP may only be truly described by more careful treatment of fluctuations. One does not presently know how such treatments will come out. Therefore, we will concentrate on the coarser features of the phase diagram; namely the first-order NC transitions with transition entropy that increases with increasing nematic range.

**IV. LANDAU THEORY**

These features follow from a free energy expression of the form

$$ F = \alpha\psi^2 + \beta\psi^4 + \gamma\psi^6 $$

$$ + \psi^6(\alpha\eta^2 + \beta\eta^4 + c\psi^2\psi^3), $$

where $\alpha = \alpha_0(T - T_c)/T_c$; $a = a_0(x_0 - x)/x_0$; $\alpha_0$, $a_0$, $\beta$, $\gamma$, $b > 0$; $c < 0$, and finally, for stability, $\gamma = -3c^2/2b > 0$. Here $x$ is the concentration of the

![Diagram](image-url)
compound exhibiting only $N$ and $C$ phases (7SS in the present case) and $x_z$ is the polycritical point concentration. We reemphasize here that this model, as that of Eq. (2), has no terms with $\eta$ alone because such models overemphasize the potential for a biaxial nematic phase. Furthermore, $\eta$ should be viewed here not as an independent order parameter in a two-order-parameter model, but as coming from the phase factor in a skewed density-wave order-parameter description which has the appropriate derivative terms in the free energy such as that of Chen and Lubensky. In fact, except for the $\psi^0$ term, Eq. (3) is essentially equivalent \cite{18} to Eq. (A1) of Ref. (14). The $\psi^0$ term is necessary to make the model complete to sixth order, and, in fact, to stabilize the $C$ phase. Without it the condition $c < 0$ drives the $C$ phase unstable when $a < \beta b / 2c$. That is, the $c \rho^0 \psi^0$ term behaves like an effectively negative $\psi^0$ term requiring the addition of a positive $\psi^0$ term for stability. The phase diagram of this model is shown in Fig. 3(c). The model gives a tricritical point on the $NC$ line at $a = \beta b / 2c$ and latent heats that increase with $x$. This latter fact is in agreement with our data, however, there is apparently no tricritical point. As Fig. 3(c) shows the model yields both a PCP, where three lines of continuous transitions meet, and the tricritical point on the $NC$ line at a distance from the PCP proportional to $\beta$, the coefficient of the $\psi^0$ term. If in fact $\beta = 0$ so that the $NA$ line is a line of tricritical points or if $\beta$ vanishes as the PCP is approached, the experimentally observed phase diagram would result. On the other hand, if $\beta$ is merely small, as has been suggested by de Gennes, \cite{9} then the PCP and the $NC$ tricritical point will be close together and it is conceivable that it would be missed within the accuracy of the present experiments or that the two points will be drawn together by the effect of fluctuations. For the latter reason we think it would be interesting to see whether a renormalization-group treatment of Chen and Lubensky’s model, modified to include the $\psi^0$ term, would result in a merging of the PCP with the $NC$ tricritical point. This of course would require an extension of renormalization-group treatment and the $\psi^0$ and second derivative terms which to our knowledge has not been done. There is another possible explanation for vanishing of the coefficient $\beta$ at the PCP. In de Gennes’s model of the $NC$ transition an infinite-component-vector order parameter is used. Therefore the PCP may be in some sense a crossover point from $n = 2$ to $n = \infty$.

Bak, Krinsky, and Mukamel \cite{19} have recently suggested the addition of a new “Landau rule” which states that if there is no stable fixed point in the $\epsilon$ expansion the transition must be first order. This may be the case for the appropriately anisotropic $n$-vector model \cite{20} as $n \to \infty$.

A crude, but we think illuminating physical picture of the $NC$ transition which supports the assumption that the effective $\psi^0$ term may change sign near the PCP is the following. X-ray evidence \cite{21} strongly suggests that there is short-range smectic-C order in the nematic phase, i.e., “skewed cybotactic groups,” which exhibit well defined tilt angles and hence finite local biaxiality. The $\psi^0$ free-energy term is phenomenologically related to the interaction between two such cybotactic groups, and this interaction is logically dependent on the relative azimuthal orientation of the fluctuations. If two fluctuations have the same tilt plane, i.e., the plane formed by the layer normal and the long molecular axis, then they should tend to merge into a larger fluctuation, increasing the free energy. Conversely, in the region between two fluctuations having different tilt planes, translational motion within one set of layers projects into interlayer motion with respect to the second cybotactic group. This implies that the effective molecular potential, i.e., the superposition of the potentials of the two fluctuations, is essentially nematic-like, with three degrees of translational freedom, in the interfluctuation region. Thus the fluctuations will not merge, but tend to destroy each other, decreasing the free energy. Assuming that the effective $\psi^0$ term is an average over all possible tilt plane orientations and that these orientations are random as required by uniaxial symmetry, the $\psi^0$ term would be negative. On the other hand, above the $A$ phase, the x-ray data indicate that the cybotactic groups are not tilted. Now any two fluctuations can grow together with at most some splay, implying a positive $\psi^0$ term. This effect accounts for the observed results and, therefore, justifies the assumption that the $\psi^0$ term changes sign near the PCP. Essentially, this justification is based on a symmetry argument which disallows a second-order $NC$ transition in the presence of short-range smectic-C order. Since the symmetry argument depends only on the existence of short-range order it seems unlikely that any uniaxial nematic to smectic-C transition will be continuous.

It begins to appear both experimentally and theoretically that the $NC$ transition must be first order on symmetry grounds.

The authors wish to thank T. Lubensky for providing us with an unpublished version of Ref. 14 prior to publication. We also wish to thank A. Sape and J. W. Doane for stimulating discussions.
NEMATIC–SMECTIC-A–SMECTIC-C POLYCRITICAL POINT...

*Research supported in part by the NSF under Grant No. DMR 74-13173.

1For a recent discussion of classification schemes for high-order critical points, see, R. B. Griffiths, Phys. Rev. B 12, 345 (1975). See Refs. 1 and 2 of that article for examples.


5R. Alben (private communication).

6The compounds used were those of a disubstituted phenyl thiolbenzoates which have the structure $X - C_7H_{14} - COS - C_6H_4 - Y$, where $X = C_8H_{17} + O$ or $Y = C_9H_{19} +$. Our binary mixture is composed of the $n = 8$, 7 homologs of the $n = 5$ homologous series and we have used the notation $\bar{n} Sm$, where the bar denotes the alkoxy end and S stands for sulphur substitution in the ester linkage. Thus we have used $\bar{8}S$ and $\bar{7}S$. See, R. Reynolds, C. Maze, and E. Oppenheim, Mol. Cryst. Liq. Cryst. (to be published) for a description of the synthesis and properties of these compounds.

7DSC-2 is a differential scanning calorimeter produced by Perkin-Elmer Corp.


17Except for the $\psi^4$ term, Eq. (A1) of Ref. (14) reduces to our Eq. (3) under the following conditions: (a) The molecular length is assumed fixed. (b) The magnitude of the order parameter is independent of spatial coordinates. Director fluctuations were also included in the model of Ref. (14), but not in expression (A1).

