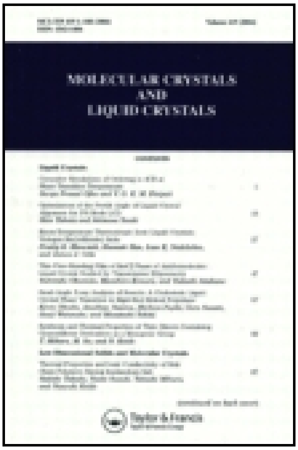

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Pressure Effects of Nematic Liquid Crystals

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Pressure Effects of Nematic Liquid Crystals. I†

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There exists a variety of important new phenomena and plenty of experimental data on the pressure effects of liquid crystals. Yet, no systematic phenomenological or microscopic theory is available. In this paper, the ordinary Landau-deGennes theory is generalized so that the free energy becomes $G = G_o(P, T) + a/2\,[T - T^*(P)]S^2 - B(P)/3\ S^3 + C(P)/4\ S^4$, $T^*(P) = T_o + bP - eP^2$. All the known pressure experiments of nematic PAA (where B and C are independent of P) are explained in one stroke and all parameters are determined. New results including reentrant I phase (I represents isotropic phase), and the independence of $T_c - T^*$ and $T^+ - T_c$ on P, etc., are predicted. Simple methods of experimental confirmation are proposed. Similar discussions on the cases of MBBA, EBBA, etc. are also given. Our theory differs from that of Lin-Keyes-Daniels but agrees better with experiments. Results related to $G_o(P, T)$ will be reported in a separate paper.

I. INTRODUCTION

Studies on the pressure effects of liquid crystals have been very active in the past ten years.[1] Pressures can lead to many interesting and fundamental phenomena. For example, pressures may induce the appearance or disappearance of certain liquid crystal phases, tricritical points, reentrant phenomena, etc. However, up to now, there exists no systematic phenomenological theory capable of explaining all (or a majority) of experimental data in a unified way. Understanding on the molecular level is minimal.[1]

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In this paper, the Landau–deGennes (LdG) theory[2] is slightly generalized to include the pressure effects. The general case of nematics is discussed. Taking PAA (*p*-azoxyanisole) as an example, detailed numerical calculations are performed and all related parameters are determined. All the known pressure experiments of PAA are explained within our theory. New measurable results are predicted and experiments to confirm them are proposed. Similar discussions are given for MBBA (*N*-*p*-Methoxy-benzylidene-*p*′-butylaniline), etc. Comparison with other theory[3] is made.

In Section II, the general theory is given. The special case of PAA is discussed in Section III in which comparison with some experiments are made [those related to the volume of the isotropic phase (I) will be present elsewhere].[4] New phenomena including reentrant I phase are predicted. Discussions on MBBA, EBBA, etc. are given in Section IV. Finally, supplements and discussions can be found in Section V.

II. THEORY

Nematic–isotropic (N–I) transition is first order in nature. The phenomenological theory of LdG[2] assumes that the Gibbs free energy G to be a polynomial expansion of the order parameter S,

$$G(P, T) = G_o(P, T) + \frac{1}{2} AS^2 - \frac{1}{3} BS^3 + \frac{1}{4} CS^4 \qquad (2.1)$$

where $G_o(P, T)$ is the free energy of I phase, A, B, C are material parameters and B, C are positive. Generally speaking, these three parameters may all be functions of pressure P and temperature T.

In the past, the case of $P =$ constant was considered. B and C are usually assumed to be independent of T and

$$A = a(T - T^*) \qquad (2.2)$$

where T^* is the supercooling temperature, a is independent of both P and T.

When P is varied, it is not entirely clear how A, B, C should be modified [see Ref. (3)]. There may be more than one way in doing this.

Here, we keep the expression of Eq. (2.2), but assume

$$T^* = T^*(P), \quad B = B(P), \quad C = C(P) \qquad (2.3)$$

and a remains a constant (independent of P and T). In other words, A is still linear in T (see Section IV). Consequently, we can adopt results obtained previously[5] and obtain

$$T_c = T^* + \frac{2}{9}\frac{B^2}{aC} \tag{2.4}$$

$$S_c = \frac{2}{3}\frac{B}{C} \tag{2.5}$$

$$S = S_o + \left(\frac{a}{C}\right)^{1/2} (T^+ - T)^{1/2} \tag{2.6}$$

where T_c is the transition temperature, S the order parameter of the nematic phase, $S_c = S(T_c)$,

$$S_o = B/2C = S(T^+) \tag{2.7}$$

$$T^+ = T^* + \frac{B^2}{4aC} \tag{2.8}$$

where T^+ is the superheating temperature.

From experimental phase diagram one observes that the $P \sim T$ curve of the N–I transition is not a straight line (See Figure 1). We therefore assume a quadratic form for T^* (P),

$$T^* = T_o + bP - eP^2 \tag{2.9}$$

Equations (2.1)–(2.3) and (2.9) constitute the basic assumptions of our theory.

1. Transition temperature $T_c(P)$

Putting Eq. (2.9) into Eq. (2.4) one obtains

$$T_c = T_o + \frac{2}{9}\frac{B^2}{aC} + bP - eP^2 \tag{2.10}$$

2. Order parameter $S(P, T)$

Substituting Eq. (2.9) into Eqs. (2.6) and (2.8) one has

$$S = S_o + \left(\frac{a}{C}\right)^{1/2} \left(T_o - T + \frac{B^2}{4aC} + bP - eP^2\right)^{1/2} \tag{2.11}$$

or

$$(S - S_o)^2 + \frac{ae}{C}(P - P_o)^2 = S_o^2 - \frac{a}{C}(T - T_o) + \frac{ab^2}{4Ce} \tag{2.12}$$

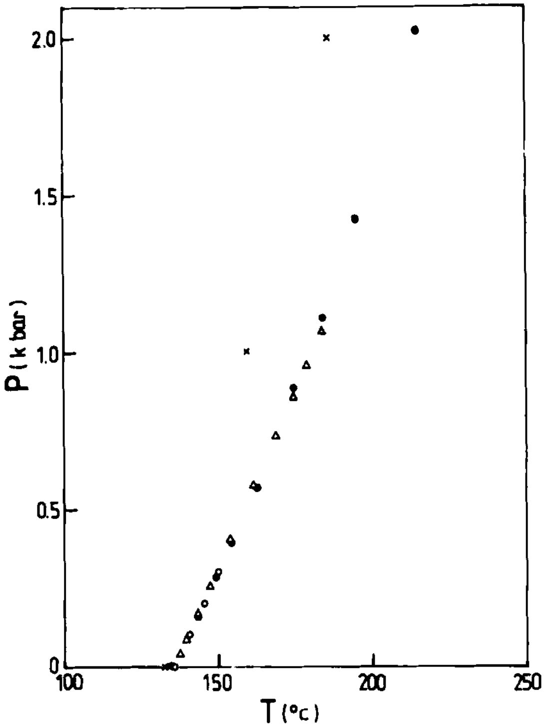

FIGURE 1 Phase diagrams of PAA. ×, ○, ●, △ represent respectively experimental results of Refs. (6, 8, 9, 10).

where

$$P_o \equiv \frac{b}{2e} \tag{2.13}$$

3. Volume V

Differentiating Eq. (2.1) with respect to P and using $\partial G/\partial S = 0$ one has the volume

$$V = \left(\frac{\partial G}{\partial P}\right)_T = V_o - ae(P_o - P)S^2 - \frac{1}{3}\frac{\partial B}{\partial P}S^3 + \frac{1}{4}\frac{\partial C}{\partial P}S^4 \tag{2.14}$$

where S is determined by Eq. (2.6) and

$$V_o = (\partial G_o/\partial P)_T \tag{2.15}$$

is the volume of I phase. Therefore, volume change at transition point is given by

$$V = V_{\mathrm{I}} - V_{\mathrm{N}} = ae(P_o - P)S_c^2 + \frac{1}{3}\frac{\partial B}{\partial P}S_c^3 - \frac{1}{4}\frac{\partial C}{\partial P}S_c^4 \qquad (2.16)$$

where $V_{\mathrm{I}} \equiv V_o(T_c)$, V_{N} is volume of N phase at T_c.

4. Isothermal compressibility K_T

The isothermal compressibility

$$K_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad (2.17)$$

where V is given by Eq. (2.14). Consequently,

$$\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial V_o}{\partial P}\right)_T + aeS^2 - \frac{1}{3}\left(\frac{\partial^2 B}{\partial P^2}\right)_T S^3 + \frac{1}{4}\left(\frac{\partial^2 C}{\partial P^2}\right) S^4$$

$$+\left[-2ae(P_o - P)S - \left(\frac{\partial B}{\partial P}\right)_T S^2 + \left(\frac{\partial C}{\partial P}\right)_T S^3\right]\left(\frac{\partial S}{\partial P}\right)_T \qquad (2.18)$$

By Eq. (2.6),

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{2}\frac{\partial}{\partial P}\left(\frac{B}{C}\right) + \left[\frac{\partial}{\partial P}\left(\frac{a}{C}\right)^{1/2}\right]_T (T^+ - T)^{1/2}$$

$$+\frac{1}{2}\left(\frac{a/C}{T^+ - T}\right)^{1/2}\left(\frac{\partial T^+}{\partial P}\right)_T \qquad (2.19)$$

It can be seen that K_T diverges as $(T^+ - T)^{-1/2}$ at $T = T^+(P)$.

5. Enthalpy change ΔH

By Eqs. (2.1) and (2.2), the enthalpy change at T_c is given by

$$\Delta H \equiv T_c\left(\frac{\partial \Delta G}{\partial T}\right)_c = \frac{a}{2}T_c S_c^2 \qquad (2.20)$$

From Eqs. (2.5), (2.10), (2.16) and (2.20), it is easy to see that the above results satisfy the Clausius-Clapeyron relation $dP/dT_c = \Delta H/T_c\Delta V$.

III. SPECIAL CASES LIKE PAA

We now consider the special case that B and C are both independent of P. Equations (2.10)–(2.13) remain unchanged. Equation (2.14) becomes

$$V = V_o - ae(P_o - P)S^2 \qquad (3.1)$$

Equation (2.16) becomes

$$V = ae(P_o - P)S_c^2 \tag{3.2}$$

By Eqs. (2.8), (2.9), (2.17)–(2.19) one obtains

$$-VK_T = \left(\frac{\partial V_o}{\partial P}\right)_T + aeS^2 - 2ae^2(P_o - P)^2 S\left(\frac{a/C}{T^+ - T}\right)^{1/2} \tag{3.3}$$

When B and C are independent of P, we can see from Eqs. (2.5), (2.10) and (2.11) that: (i) S_c is a constant independent of P; (ii) $T_c \sim P$ is a parabola; (iii) for fixed T, $S \sim P$ is an ellipse; (iv) for fixed S, $P \sim T$ is a parabola.

In our opinion, PAA is a real example of this special case.

Comparison with experiments

1. In fact, experiments by Deloche *et al.*[6] and McColl[7] show that S_c is independent of P, as predicted by (i) above.

2. For the $T_c \sim P$ curve of PAA, there exist 4 experiments by Hulett,[8] Deloche *et al.*,[6] Spratte and Schneider,[9] and Stishov *et al.*,[10] respectively. See Figure 1. With the exception of data by Deloche *et al.*[6] results by the other three groups are pretty consistent with each other. The range of pressure measured is the widest in the case of Spratte and Schneider.[9] We therefore use the experimental data of Ref. (9) in our analysis. The $P \sim T$ curve from Ref. (9) is found to be described very well by our Eq. (2.10). The parameters in Eq. (2.10) are obtained by a least square fit resulting in

$$b = 4.98 \times 10^{-2}\,^\circ\mathrm{C\ bar}^{-1}$$

$$e = 5.28 \times 10^{-6}\,^\circ\mathrm{C\ bar}^{-2}$$

$$T_o + \frac{2}{9}\frac{B^2}{aC} = 135.3\,^\circ\mathrm{C} \tag{3.4}$$

The theoretical $P \sim T$ curve is represented by the solid line in Figure 3.

3. In order to check Eq. (2.12) the measured $S = S(P, T)$ curves by McColl[7] [Figure 1 of Ref. (7)] are examined. For fixed T, the $S \sim P$ curves indeed look like ellipses. For a more convenient quantitative comparison Figure 1 of Ref. (7) is redrawn as $T \sim P$ (S fixed) curves in our Figure 2.

By Eq. (2.12), when S is fixed, $T \sim P$ should be a parabola. Equation (2.12) may be rewritten as

$$\frac{ae}{C}(P - P_o)^2 = -\frac{a}{C}(T - T_1) \tag{3.5}$$

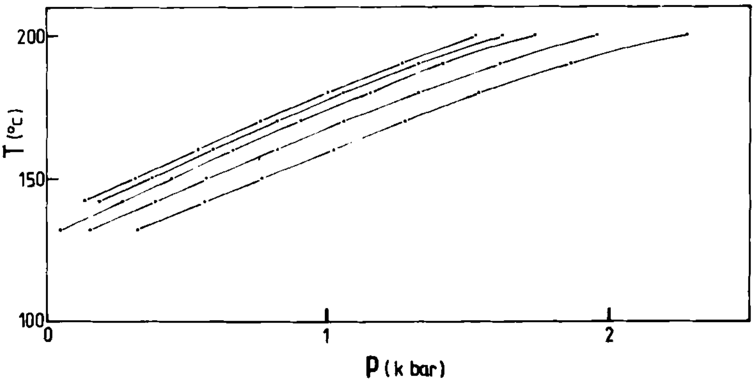

FIGURE 2 $T \sim P$ (S fixed) curves of PAA. Solid points are read from Figure 1 of Ref. (7). $S = 0.6, 0.55, 0.50, 0.45, 0.37$ respectively for the five curves starting from the lowest one.

and

$$T_l = T_l(S) \equiv T_o + \frac{b^2}{4e} + \frac{C}{a} S_o^2 - \frac{C}{a}(S - S_o)^2 \qquad (3.6)$$

In other words, if the curves in Figure 2 really satisfy Eq. (3.5), then by suitable displacements along the T axis these curves can be made to coincide with each other. This is indeed found to be the case. As shown in Figure 3 all the curves in Figure 2 collapse into the $T \sim P$ curve with $S = 0.37$ after displacements parallel to the T axis. In McColl's experiment,[7] $S_c = 0.37$. The $T \sim P$ curves with $S = 0.37$ in Figures 2

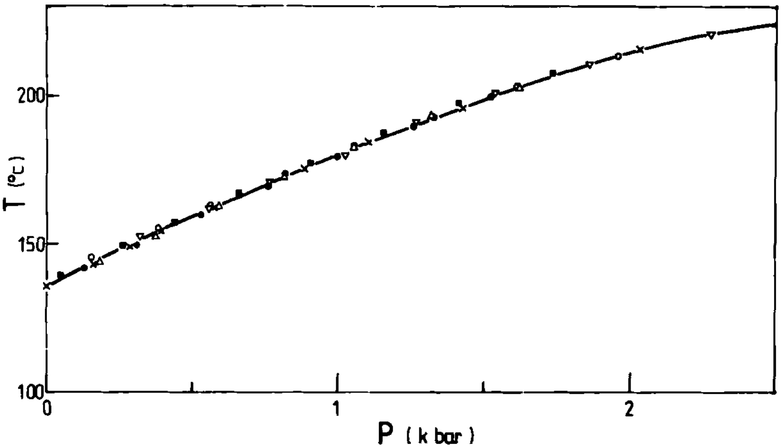

FIGURE 3 $T \sim P$ curves obtained by shifting the curves in Figure 2 along the T axis. ∇, O, ■, Δ, ● correspond to the curves in Figure 2 with $S = 0.60, 0.55, 0.50, 0.45, 0.37$, respectively. Solid line is theoretical result from Eqs. (2.10) and (3.4). The material is PAA.

and 3 are in fact the transition line $T_c(P)$. When the T_{NI} points from Figure 6 of Ref. (9) are drawn in our Figure 3 (represented by x), they are found to fall basically on a smooth line. In addition, the theoretical $T_c(P)$ curve (represented by the solid line) from Eqs. (2.10) and (3.4) is found to agree very well with these points. This shows that the $T_c(P)$ data of Spratte and Schneider[9] are consistent with the experiments of McColl.[7] More important, the experimental data $S(P, T)$ of PAA indeed satisfy Eq. (3.5).

In the experiments of Deloche *et al.*[6] for PAA, $S_c = 0.40$. Since the $T_c(P)$ points from Ref. (6) deviate too much from those used here (see Figure 1) and for the sake of consistency in data analysis, the S_c value of McColl[7] is adopted here.

For further checking of Eq. (3.6), by Eqs. (2.5), (2.7) and $S_c = 0.37$[7] we find $S_o = \frac{3}{4} S_c = 0.278$. In Figure 4, $(S - S_o)^2 \sim T_2$ is plotted. Here, T_2 is the intercept of $T \sim P$ curve on the T axis ($P = 0$) in Figure 2. By Eq. (2.12) [or Eqs. (3.5), (3.6)], when P is fixed $(S - S_0)^2$ should vary linearly with T, with slope $-a/C$. Figure 4 basically agree with this theoretical result. From the best linear fit to the points in Figure 4 we find

$$a/C = 4.90 \times 10^{-3}\ ^{\circ}\mathrm{C}^{-1} \tag{3.7}$$

In short, Eq. (2.12) can explain very well the experimental curves $S(P, T)$[7] of PAA. To our knowledge, there is no quantitative or even qualitative explanations of McColl's experiments since its publication in 1972.

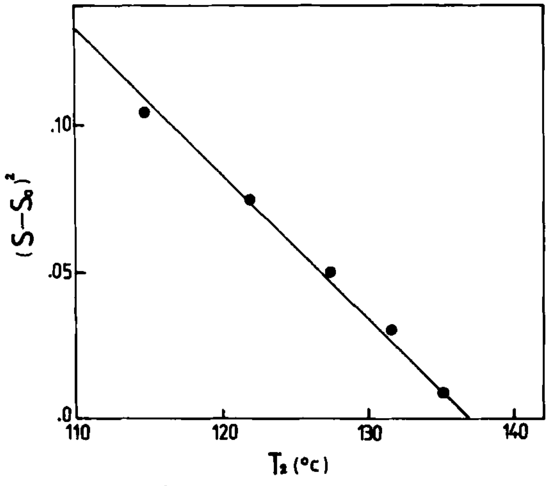

FIGURE 4 Relation $(S - S_o)^2 \sim T_2$ of PAA. T_2 is the intercept of $T \sim P$ curve on the T axis in Figure 2. The straight line is the best linear fit through the points.

4. To check Eq. (3.2) we note first from Eqs. (2.13) and (3.4) that

$$P_o = 4.72 \text{ kbar} \tag{3.8}$$

and hence ΔV should vanish at $P = 4.72$ kbar. Experimentally for PAA, $\Delta V \sim P$ has been measured by Stishov *et al.*[10] and Baskakov *et al.*,[11] respectively. When $P = 1$ bar, $\Delta V = 0.69$ cm^3 mol^{-1} by Ref. (10) which is close to $\Delta V = 0.81$ cm^3 mol^{-1} of Ref. (12). On the other hand, $\Delta V = 22$ cm^3 mol^{-1} from Ref. (11) deviates very much from the previous two values. Also, when ΔV of Ref. (11) is extrapolated, one finds $\Delta V = 0$ at $P = 2.45$ kbar ($T_c = 218$°C) which is quite different from what we expect above. In contrast, data from Ref. (10) is consistent with the predictions of Eq. (3.2) (see Figure 5). The slope of straight line in Figure 5 should be $-aeS_c^2$. Using $S_c = 0.37$[7] and the value of e from Eq. (3.4) we find

$$a = 2.10 \times 10^8 \text{ erg mol}^{-1}\,{}^\circ\text{C}^{-1} \tag{3.9}$$

It is worth to point out that ΔV from Refs. (10) and (11) (especially the latter) are both linear in P, in agreement with Eq. (3.2).

5. By Eqs. (2.1)–(2.3) and (2.9), one sees that there are 6 material parameters (a, b, e, T_o, B, C). From $S_c = 0.37$[7] and Eq. (2.5), we obtain

$$B/C = 0.555 \tag{3.10}$$

Using Eqs. (3.4) and (3.7) we have

$$T_o = 121.3^\circ\text{C} \tag{3.11}$$

By Eqs. (3.7), (3.9) and (3.10),

$$C = 4.28 \times 10^{10} \text{ erg mol}^{-1} \tag{3.12}$$

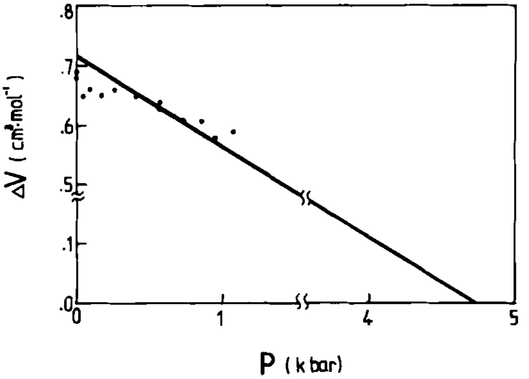

FIGURE 5 Volume change ΔV vs. pressure P of PAA. The points are experimental data;[10] the straight line theoretical result of Eq. (3.2).

$$B = 2.37 \times 10^{10} \text{ erg mol}^{-1} \tag{3.13}$$

At this point, all the 6 parameters have been found (Table I). The value $a = 0.94 \times 10^6$ erg cm^{-3} °C^{-1} agrees very well with that ($a \simeq 10^6$ erg cm^{-3} °C^{-1}) assumed by Imura and Okano[13] in their calculation of specific heat of PAA in the I phase.

6. The data of $\Delta H \sim P$ in Ref. (10) are derived from those of ΔV using the Clausius-Clapeyron relation. Consequently, they automatically satisfy our Eq. (2.20). Equations (3.1), (3.3) and other results involving the specific forms of V and $V_0(P, T)$ will be discussed in a separate paper.[4]

Predictions In the following, we shall present a few predictions from our theory as well as simple experimental methods of verification. For other predictions, see Ref. (4).

7. By Eqs. (2.4) and (2.8), $T^+ - T_c = \frac{1}{8}(T_c - T^*)$. In PAA, since a, B and C are all independent of P and T, it then follows that both $T_c - T^*$ and $T^+ - T_c$ are also independent of P and T.

For verification, one only has to put PAA in a liquid crystal cell, the pressure of which can be varied and repeat the usual experiments that measure T^* (e.g. measuring in I phase the magnetic birefringence Cotton-Mouton coefficient,[14,15] the electric birefringence Kerr coefficient,[16] light scattering,[14] etc.) or T^+ (nuclear magnetic resonance measurements).[17]

8. The part of curve represented by broken line in Figure 6 is obtained by extrapolation when the experimental part (solid line) of the phase diagram of PAA is fitted with parabola [see Eq. (2.10) and Table I]. From Figure 6, it can be seen that the N-I transition line intercepts the N-X (X represents solid phase) transition line at point D ($P = 6.37$ kbar, $T = 238$°C) and the point on the N-I line with the highest temperature is W ($P = 4.72$ kbar, $T = 251$°C). Therefore, if the temperature of PAA liquid crystal is fixed between 238–251°C and the

TABLE I

Parameters of PAA

$a = 2.10 \times 10^8$ erg mol^{-1} °C^{-1}
$b = 4.98 \times 10^{-2}$ °C bar^{-1}
$e = 5.28 \times 10^{-6}$ °C bar^{-2}
$T_0 = 121.3$°C
$B = 2.37 \times 10^{10}$ erg mol^{-1}
$C = 4.28 \times 10^{10}$ erg mol^{-1}

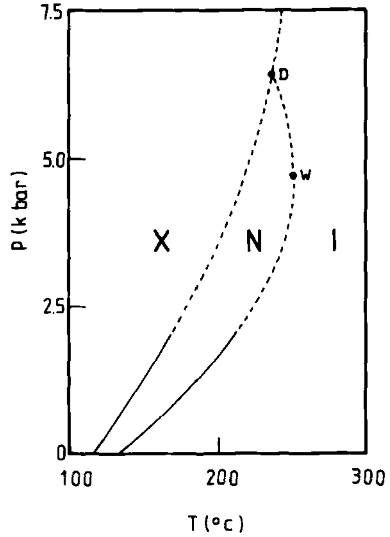

FIGURE 6 Phase diagram of PAA. I: isotropic phase, N: nematics, X: solid phase. The solid lines are experimental results.[9] The broken lines are extrapolations when the solid lines are described by parabolas. Point D corresponds to $P = 6.37$ kbar, $T = 238°\text{C}$; W: $P = 4.72$ kbar, $T = 251°\text{C}$.

pressure is increased slowly, PAA will go through the three phases I–N–I. In other words, at high pressure ($P > 4.72 \sim 6.37$ kbar), I phase reappears. The properties of this reentrant I phase will be basically the same as those of the I phase at low pressure since they belong to the same connected region in the phase diagram.

To verify this prediction of the reentrant I phase, the most direct method is to adopt the procedure mentioned above, viz., fix the temperature of PAA and change the pressure. Under the illumination of light, the I phase is clear and the N phase is milky-like and can be distinguished easily.

A more indirect method is to measure the volume change ΔV. At point W, $\Delta V = 0$; on the line DW, $\Delta V < 0$ [see Eq. (3.2), Figure 5 and Ref. (4)]. For other possible experiments, see paragraph 10 below.

It is worth to point out that since $T_c - T^*$ is independent of P one may obtain the curve T^* (P) by simply shifting the N–I line in Figure 6 to the left by an amount ($T_c - T^*$). If the I phase can exist metastably between $T_{\text{NI}}(P)$ and $T^*(P)$ ($T_{\text{NI}} = T_c$) then in a small temperature range ($T_c - T^*$) on the N-phase side of W, when the temperature is fixed and the pressure is varied one may obtain only the I phase. However, for T smaller than 251°C $- (T_c - T^*)$ but greater than 238°C one should always get I–N–I transitions. Problems related to the numerical value of $T_c - T^*$ will be discussed in Section V.

In Figure 6, the procedure of extrapolation from a small sect of experimental points is not unquestionable. However, from the good agreement between theory and experiments presented in paragraphs 1–6 above we have reason to believe that it is not completely incidental that $T_{NI}(P)$ can be described by a parabola of Eq. (2.10). The important point is that even if $T_{NI}(P)$ can no longer be represented by a parabola (e.g. an ellipse) at high pressure, Figure 6 and the resulting deductions are still basically correct. The reason is that since the experimental portion of $T_{NI}(P)$ is convex in the direction of rising temperature, there certainly will exist a turning point like W and hence a reentrant I phase. The example of PAA shows that the pressure corresponding to this turning point needs not to be very high.

In fact, in the PAA experiments of Deloche *et al.*, [6] for $T \sim 210$°C and $P \sim 3$ kbar, the rate of increase of T_c has obviously reduced very much. The $P \sim T$ curve in Figure 1 starts to bend towards the left, in agreement with the prediction of Figure 6. Similar behavior was observed in the experiments of Spratte and Schneider[9] at $T \sim 227$°C and $P \sim 2$ kbar. These authors attributed this effect to the possible impurities coming from the decomposition of the liquid crystal sample. But this is purely a speculation. According to our theory, the reduction of T_c is an inevitable consequence of the increase of pressure. Experimental verifications are desperately needed.

9. From Figure 6, it can be seen that when $P > 6.37$ kbar and the pressure is fixed, then PAA may change directly from I phase to X phase upon cooling. The N phase does not appear.

The interesting point is that in the N–A (A represents smectic A) transition of liquid crystal CBOOA (*N*-*p*-cyano-benzulidene-*p*-octyloxyaniline) Keyes and Daniels[18] have observed something very similar to our two predictions above (in paragraphs 8 and 9).

10. When light passes through a liquid crystal sample, the intensity of transmitted light $I_t = I_o e^{-\tau L}$, where L is length of sample, I_o a constant. Also, $\tau \sim T/A$ [A defined by Eq. (2.1)].[3] Therefore, τ may be determined by light scattering measurements. We plot in Figure 7 theoretical curves of $A(P, T)$ for PAA according to Eqs. (2.2), (2.9) and Table I. Note that for T fixed, the curve $A \sim P$ bends into different directions in the regions of $P < P_o$ and $P > P_o$ [value of P_o given by Eq. (3.8)], respectively. A vanishes at two points, $P = \mathrm{P}_o \pm [P_o^2 + (T_o - T)/e]^{1/2}$. For $T > T^*(P_o) = T_o + b^2/4e$, $A > 0$.

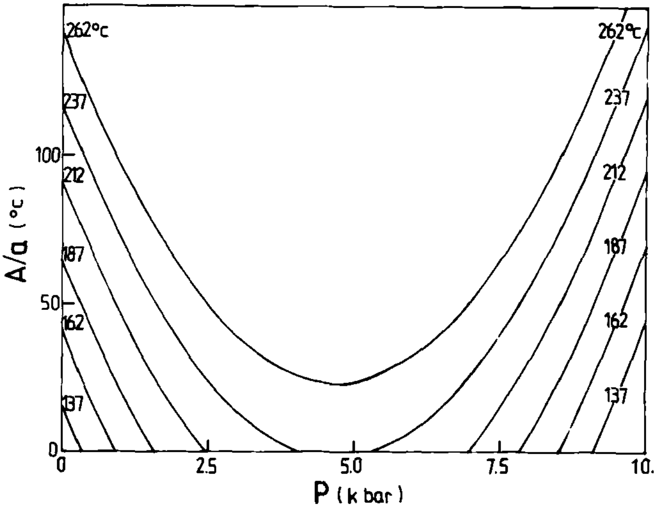

FIGURE 7 Theoretical curves of $A(P, T)$ of PAA.

In fact, $A(P, T)$ can be measured through pretransitional effects in the I phase near T_c, which include flow birefringence, magnetic birefringence, optical or electric Kerr effect, nuclear magnetic resonance, light scattering, etc.[19] To confirm the results of Figure 7 one only has to repeat these experiments under various pressure.

To our knowledge, there exists now no experimental data of PAA related to Figure 7 (for the case of MBBA and related materials see Section IV). These experiments should be very meaningful.

IV. CASES LIKE MBBA

For liquid crystals like MBBA and 5CB, since S_c depends on P [see Figure 26 of Ref. (1)][20] it is obvious that the assumption of B and C being P-independent no longer holds [see Eq. (2.5)], in contrast to the case of PAA. For cases like MBBA we believe that the theory in Section II is still valid provided the functional forms of $B(P)$ and $C(P)$ are suitably chosen. For example, with the assumption

$$B = \frac{\gamma}{\alpha(\bar{P} - P)}, \quad C = \frac{\gamma}{\alpha^2(\bar{P} - P)^2} \qquad (4.1)$$

where α, γ, $\bar{P}$ are constants (independent of P and T), $\alpha > 0$, $\bar{P} > 0$, Eq. (2.5) then gives

$$S_c = \frac{2}{3}\alpha(\bar{P} - P) \tag{4.2}$$

S_c decreases linearly with P, in agreement with experiments[20] of MBBA and 5CB. In addition, by Eq. (2.4), we have $T_c = T^* + \frac{2}{9}\gamma/a$ which when combined with Eq. (2.9) results in a parabola for $T_c(P)$, again in agreement with experimental results of MBBA, EBBA, PEBAB, nCB, etc.[9,21] In this paper, we do not intend to discuss the numerical values of these material parameters. Yet, comparing Figure 26 of Ref. (1) with our Eq. (4.2) one sees that $\bar{P}$ is the interception of S_c with the P axis. For MBBA, we have $\bar{P} \sim 17.3$ kbar. Consequently, under the usual experimental conditions (where P is smaller than a few kbar) B and C in Eq. (4.1) do not diverge with respect to P and Eq. (4.1) can be used.

In fact, Eq. (4.1) is not the only possible form of B and C. For liquid crystals like MBBA, the only requirements are that B/C be linear in P and B^2/C be quadratic in P.

We now discuss problems related to A. By Eqs. (2.2) and (2.9),

$$A = A(P, T) = a(T - T_o - bP + eP^2) \tag{4.3}$$

which must have the forms shown in Figure 7. From Figure 5 of Ref. (3), the experimental curve $\tau^{-1} \sim P$ (T fixed) of EBBA is not exactly a straight line ($\tau^{-1} \sim T/A$, see paragraph 10 of Section III). Our theoretical result of Eq. (4.3) or Figure 7 is obviously more close to experiments than the theoretical straight line of Ref. (3). In Ref. (3), Lin *et al.* assume

$$A = a(T)\,[P^*(T) - P], \quad B = (T), \quad C = C(T) \tag{4.4}$$

and hence obtain a straight line for $A \sim P$, differing from our Eq.(4.3). From the above discussions, we believe that Eq. (4.3) is more reasonable than Eq. (4.4). More important, the assumption of Eq. (4.3) and (2.3) reduces immediately to the usual result of constant pressure when $P =$ constant while Eq. (4.4) does not.

Similar to the reasonings presented in paragraph 8 of Section III, since the $T_c(P)$ curve of materials like MBBA can also be approximated by parabola,[9,21] there may also appear reentrant I phase in these materials.

V. DISCUSSIONS

1. Our theory is based on the assumptions in Eqs. (2.1)–(2.3) and (2.9). In comparison with Ref. (3) [see Eq. (4.4)], our assumptions

are more reasonable and more close to experiments (see Section IV). When applied to liquid crystals like PAA our theory can explain very well experimental curves such as $T_c(P)$, $S_c(P)$, $S(P, T)$ and $\Delta V(P)$ (see Section III). In fact, our theory can also explain other experimental results of K_T, $P(V, T)$, $S(V, T)$, etc. [see Ref. (4)]. All these pressure experiments of PAA, to our knowledge, have not been explained theoretically before in any systematic way. As we pointed out in Section IV, our theory is also applicable to other nematic materials.

In our theory, T^* is assumed to be quadratic in P in Eq. (2.9). And T_c becomes quadratic in P only when B^2/C is also the case [see Eq. (2.10)]. T^* is the source and T_c the consequence. This point is very important. Therefore, if one starts from assumption of $T_c(P)$ it is not easy to develop a theory. We note that in their investigation of pressure effects of nCB, Shashidhar and Venkatesh[21] have assumed a parabolic empirical form for $T_c(P)$.

2. In reentrant phenomena of thermotropic liquid crystals, only the types of N–A–N or A–N–A–N have been observed[22,23] so far. Hence, the reentrant phenomenon I–N–I predicted here (in paragraph 8 of Section III and Section IV) is of a new variety, the method of observation of which is not complicated at all. In solution of PBLG, reentrant I–N*–I (N* represents cholesterics) has been predicted[24] but this is in the domain of lyotropic liquid crystals.

3. By calculation using Eq. (2.4) and Table I, we obtain $T_c - T^* = 13.9°\mathrm{C}$ for PAA, compared to the experimental value of ca. 3.3°C. From Section I, one can show that $S(T^*)/S(T_c) = 3/2$, irrespective of P. The discrepancy of this result at constant pressure with experiments is well-known.[5] Our theory does not succeed in avoiding this contradiction, which is the source of the discrepancy between the calculated $T_c - T^*$ and experiments above. To solve this problem, one possible way is to assume $a = a(T)$ [may be with $B = B(P, T)$, $C = C(P, T)$ also] but then the LdG theory will become too complicated to be attractive.

4. In the usual application of the Landau theory, one makes a temperature expansion near T_c at constant pressure resulting in $A(P, T) = a(T - T^*)$. In fact, if one aims at the whole $P \sim T$ plane of the phase diagram one should have $A(P, T) = f(P, T)\mathcal{A}(P, T)$ where $f(P, T)$ is an arbitrary function and $\mathcal{A}(P, T^*) = 0$, $T^*(P)$ the supercooling curve in the phase diagram. In our theory, $f(P, T) =$ constant and $\mathcal{A}(P, T)$ is defined by Eq. (4.3) corresponding to the parabolic N–I transition line. The general form of $A(P, T)$ discussed above will be useful in discussing other phase transition phenomena including reentrant phenomena.[22,23]

5. A more comprehensive conclusion in regard to the pressure effects of nematics will be given in Ref. (4).

In passing, we note that in describing the second order reentrant N–A (A represents smectic A) phase transition Pershan and Prost[25] used a Landau theory starting with a Helmholtz free energy in which the transition temperature is quadratic in the density. In contrast, in our work the N–I transition is first order and we start from a Gibbs free energy. Also, Clark,[26] and Klug and Whalley[27] have derived an elliptic shape of the A–N phase boundary by a quadratic expansion in T and P of the change of the Gibbs free energy in which the order parameter is not involved [differing from the case of Ref. (25)].

References

1. S. Chandrasekhar and R. Shashidhar, in *Adv. in Liq. Cryst.*, (ed. H. G. Brown) Vol. 4 (1980), p. 83.
2. P. G. deGennes, *Phys. Lett.*, **30A**, 454 (1969); *Mol. Cryst. Liq. Cryst.*, **12**, 193 (1971).
3. W. J. Lin, P. H. Keyes and W. B. Daniels, *J. Physique*, **41**, 633 (1980).
4. Liu Jiagang and Lin Lei, the following paper.
5. Lin Lei and Cai Jundao, *Scientia Sinica*, **22**, 1258 (1979).
6. B. Deloche, B. Cabane and D. Jerome, *Mol. Cryst. Liq. Cryst.*, **15**, 197 (1971).
7. J. R. McColl, *Phys. Lett.*, **38A**, 55 (1972).
8. G. A. Hulett, *Phys. Chem.*, **28**, 629 (1899).
9. W. Spratte and G. M. Schneider, *Ber. Bunsenges. Phys. Chem.*, **80**, 886 (1976).
10. S. M. Stishov, V. A. Ivanov and V. N. Kachinskii, *JETP Lett.*, **24**, 297 (1977).
11. V. Ya. Baskakov, V. K. Semenchenko and V. M. Byankin, *JETP*, **39**, 383 (1974).
12. W. Maier and A. Saupe, *Naturforsch*, **15(a)**, 287 (1960).
13. H. Imura and K. Okano, *Chem. Phys. Lett.*, **17**, 111 (1972).
14. Y. W. Stinson and J. D. Litster, *Phys. Rev. Lett.*, **25**, 503 (1970).
15. K. Muta *et al*, *Jpn. J. Appl. Phys.*, **18**, 2093 (1979); B. Malraison *et al*, *Solid State Commun.*, **31**, 843 (1979).
16. B. R. Ratna and R. Shashidhar, *Mol. Cryst. Liq. Cryst.* (to be published).
17. R. Y. Dong and E. Tomchuk, *Phys. Rev.* **A17**, 2062 (1978); R. Y. Dong, *Phys. Rev.* **A21**, 1064 (1980).
18. P. H. Keyes and W. B. Daniels, *Phys. Lett.*, **49A**, 453 (1974).
19. P. G. deGennes, *The Physics of Liquid Crystals*, Clarendon, Oxford (1974); S. Chandrasekhar, *Liquid Crystals*, Cambridge U. Press (1977).
20. R. G. Horn, Ph. D. Thesis, Cambridge University (1976).
21. R. Shashidhar and G. Venkatesh, *J. Physique*, **40**, C3-396 (1979).
22. P. E. Cladis, in *Liquid Crystals*, ed., S. Chandrasekhar, Heyden, London, 1980; J. Prost, in *Liquid Crystals of One- and Two-Dimensional Order*, eds., W. Helfrich and G. Heppke, Springer-Verlag, Berlin (1980).
23. Lin Lei, *Progress in Liquid Crystal Physics*, see Tan Manqi, Ding Xueshan, Lin Lei (transl. and eds.), *Liquid Crystals*, Popular Science Press (1983).
24. V. T. Rajan and C. -W. Woo, *Phys. Rev.*, **A21**, 990 (1980).
25. P. S. Pershan and J. Prost, *J. Physique*, **40**, L-27 (1979).
26. N. A. Clark, *J. Physique*, **40**, C3-345 (1979).
27. D. D. Klug and E. Whalley, *J. Chem. Phys.*, **71**, 1874 (1979).