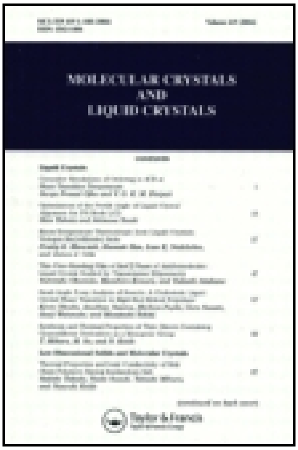

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Microscopic Theory of Reentrant Behavior in Liquid Crystals[†]

L. V. Mirantsev [a]

[a] Academy of Sciences of Azerbaijan SSR, Baku, OKB "Register," Institute of Physics, 370143, USSR

Version of record first published: 20 Apr 2011.

To cite this article: L. V. Mirantsev (1986): Microscopic Theory of Reentrant Behavior in Liquid Crystals[†] , Molecular Crystals and Liquid Crystals, 133:1-2, 151-168

To link to this article: http://dx.doi.org/10.1080/00268948608079568

Mol. Cryst. Liq. Cryst., 1986, Vol. 133, pp. 151–168
0026-8941/86/1332-0151/$20.00/0

Printed in the United States of America

Microscopic Theory of Reentrant Behavior in Liquid Crystals†

L. V. MIRANTSEV

OKB "Register," Institute of Physics, Academy of Sciences of Azerbaijan SSR, Baku 370143, USSR

(*Received September 15, 1984*)

The extraordinary phase sequences, namely nematic (N) → smectic A(SA_1) → reentrant nematic (N_{rc}) and N → S_{A_1} → N_{rc} → reentrant smectic A($S_{A_{rc}}$) occur with decreasing temperature in strongly polar liquid crystals (LC). The period of the smectic density wave in intermediate S_{A_1} phase is not commensurate with the molecular length l but varies for different compounds from 1.1 l up to 1.6 l and the period of the density wave in the $S_{A_{rc}}$ phase is almost equal to molecular length (i.e. 0.99 l). In order to explain this behavior it is assumed that the pairing of molecules with antiparallel dipole moments takes place in polar LCs. In the present paper, in a mean field approximation, we considered LCs consisting of dimers (paired molecules) and monomers (unpaired molecules) in which two density waves with periods equal to the length of the dimer (d) and the length of monomer (l), respectively, may exist. The free energy F of such LCs is expressed in terms of amplitudes of these density waves, temperature T and dimer concentration X_D. The regions of existence of each density wave on the (X_D, T) plane are found by minimization of the free energy F. The conditions of occurrence of N_{rc} and $S_{A_{rc}}$ phases are determined and also the heat capacity discontinuities at the N → S_{A_1} and S_{A_1} → N_{rc} second order transitions are calculated. These heat capacity discontinuities are about one or two orders smaller than those at the N → S_A transitions in ordinary LCs. It is also shown that this theory accounts for the S_A → $S_{A'}$ transition in compounds with a bilayer S_A phase.

I. INTRODUCTION

The extraordinary phase sequence, namely nematic (N) → smectic A(S_A) → reentrant nematic (N_{rc}) occurs with decreasing temperature in some liquid crystals (LC) consisting of molecules with strongly

---

†Accepted but not presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.

polar end group (CN or NO_2). This sequence may be observed in binary mixtures,[1] in pure compounds at high pressure,[2] and, finally, even in pure compounds at atmospheric pressure.[3] In all LCs studied up to now, the period d of the density wave in the intermediate S_A phase is not commensurate with molecular length l, but varies for different compounds from 1.1 l up to 1.6 l (Refs. 4, 5). Furthermore, a more complicated phase sequence, namely, N → S_A → N_{re} → reentrant smectic A($S_{A_{re}}$) occurs[3,6] in some polar compounds, such as 4-n-octyloxy-benzoyloxy-4′-cyano stilbene ("T8"). An X-ray study[7] of this compound has shown that the period of the density wave in the high temperature partially bilayer S_A phase is weakly dependent on temperature and equal to about 1.3 to 1.4 l, whereas the period of the density wave in the $S_{A_{re}}$ phase is almost equal to molecular length (i.e $\approx 0.99\ l$).

It should be noted, that another extraordinary phenomenon, namely, a direct transition between two S_A phases ($S_A \rightarrow S_{A'}$) also occurs[8] in some strongly polar LC. An X-ray study[9] of such LC has shown that there is only one density wave with the period equal to molecular length l in S_A phase, whereas two density waves with the period equal to l and 1.95 l, respectively, coexist in $S_{A'}$ phase.

In order to explain the occurence of N_{re} phase de Jeu and Longa[10] proposed a microscopic model based on the assumption of the pairing of molecules with antiparallel dipole moments in strongly polar LCs, consisting of molecules with large permanent dipole moments (~ 4,5 D). Each pair (dimer) is a completely symmetrical unit (its total dipole moment is equal to zero) with the bulk core formed of overlapped hard aromatic parts of molecules and two flexible alkyl chains at the ends. The length of dimer may vary from molecular length l up to 2 l. Dimer concentration increases with decreasing temperature and above a certain concentration an S_A phase with the layer periodicity equal to length of dimer can be formed (according to model unpaired monomers also take part in the formation of this S_A phase). Further an increase of the dimer concentration with the decreasing temperature gives rise to enhancement of the repulsive forces between their hard cores that may result in destruction of the smectic layers and appearance of the N_{re} phase.

It is probable that de Jeu and Longa's model gives a key to the understanding of the reentrant behavior in LCs at a microscopic level. However, their theory[10] only allows a determination of the transitional points (N → S_A and S_A → N_{re}) and gives no information on such an important characteristic of the transition such as the heat capacity discontinuity. Also this theory cannot explain the occurrence of an S_A phase with layer periodicity different to that in the intermediate S_A phase and does not take into account the influence of the exact shape of the temperature dependence on the dimer concentration for the phase sequences.

The main purpose of present paper is to overcome these theoretical limitations. Also will be shown, the theory is applicable to the description of the direct $S_A \rightarrow S_{A'}$ transition.

II. ONE-PARTICLE DESCRIPTION OF N → S_A TRANSITION IN MONOMERS AND DIMERS MIXTURE

According to de Jeu and Longa's model liquid crystals consisting of polar molecules can be considered as a mixture of monomers (M) and dimers (D), interacting through the general two-particle potential[10]

$$V_{AB}(\Omega_A,\Omega_B,\vec{r}_{AB}) = \begin{cases} \infty & \text{if } |\vec{r}_{AB}| < \xi_{AB} \\ -V_{AB}(\Omega_A,\Omega_B,\vec{r}_{AB}) & \text{if } |\vec{r}_{AB}| \geqslant \xi_{AB} \end{cases} \qquad (1)$$

where ξ_{AB} is a distance of the closest approach of A,B ($A,B = M,D$) $\Omega_A = (\theta_A,\varphi_A)$ are the angles defining the orientation of the long axis of a molecule A with respect to a given coordinate system and $\vec{r}_A$ is a vector defining the position of its center of mass, while $\vec{r}_{AB} = \vec{r}_A - \vec{r}_B$.

The potential Eq (1) is composed of a hard-core repulsion for $|\vec{r}_{AB}| < \xi_{AB}$ and an attractive part $-V_{AB}$ $(\Omega_A,\Omega_B,\vec{r}_{AB})$ for $|\vec{r}_{AB}| \geqslant \xi_{AB}$. According to a generally accepted notion[11] repulsive forces destabilize the smectic phase whereas attractive forces are responsible for its stability.

If one assumes, that each molecule A feels some homogeneous internal mean field and the molecular state is defined by a one-particle distribution function $f_A(\vec{r}_A,\Omega_A)$,[11,12] then the orientational free energy F of mixture of monomers and dimers is given by

$$F = U - TS_r, \qquad (2)$$

$$U = -(1/2)(N^*)^2 \sum_{A,B=M,D} X_B X_A (4\pi V)^{-2} \cdot \iint d\Omega_A d\Omega_B d\vec{r}_A d\vec{r}_B f_A V_{AB} f_B, \qquad (3)$$

$$\text{and} \quad S_r = -K_B N^* (4\pi V)^{-1} \sum_{A=M,D} X_A \int d\Omega_A d\vec{r}_A f_A \ln f_A, \qquad (4)$$

where U is the internal energy, S_r—orientational entropy, $X_M = N_M/N^*$, $X_D = 1 - X_M = N_D/N^*$ are the monomer and dimer concentrations, respectively, N_M and N_D are the numbers of monomer and dimers, $N^* = N_M + N_D = N/(1 + X_D)$ is the total number of particles, $N = N_M + 2N_D$ is the total number of molecules, V is the volume of the system, T is the absolute temperature and K_B is the Boltzman constant.

In order to describe the nematic → smectic A transition in this mixture it is necessary to choose an appropriate expression for the one-particle distribution function $f_A(\vec{r}_A, \Omega_A)$ (where $A = M, D$) taking into account symmetry of both the N and S_A phases.

In the mean-field approximation the function $f_A(\vec{r}_A, \Omega_A)$ has the form:[11]

$$f_A(Z_A, \theta_A) = \frac{\{\exp[(-V_A^{(1)}(\cos\theta_A) - V_A^{(2)}(\cos\theta_A, Z_A))|K_BT]\}}{\int d\vec{r}_A d\Omega_A \exp[(-V_A^{(1)}(\cos\theta_A) - V_A^{(2)}(\cos\theta_A, Z_A))|K_BT]} \tag{5}$$

where $V_A^{(1)}(\cos\theta_A)$ is the part of the mean field defining orientational ordering in the N phase, $V_A^{(2)}(\cos\theta_A, Z_A)$ is that part of the mean field defining translational ordering along the Z axis in the S_A phase and θ_A is the polar angle between the long molecular axis and the direction of preferable alignment (i.e. the director) $\vec{n}$ coinciding with the Z axis. The relation between the one-particle potential $(V_A^{(1)}(\cos\theta_A) + V_A^{(2)}(\cos\theta_A, Z_a))$ and the two-particle potential (1) is given by

$$V_A(\cos\theta_A, Z_A) = V_A^{(1)} + V_A^{(2)} = \sum_{B=M,D} N^* X_B \int d\vec{r}_B d\Omega_B V_{AB} f_B \tag{6}$$

and the internal energy of system U is given by

$$U = -(N^*|2V) \sum_{A=M,D} X_A \int f_A V_A d\vec{r}_A d\Omega_A. \tag{7}$$

Further let us assume that for our system the difference between the temperatures of the isotropic (I) → N and N → S_A transitions is large enough and the orientational order in the mixture of monomers and dimers is sufficiently established. Then we can consider this system in the frame work of the saturated McMillan model,[10] i.e. we shall apply the approximation of ideal orientational order which leads to the following expression for $f_A(\vec{r}_A,\Omega_A)$:

$$f_A(Z_A, \theta_A) = \delta(\cos^2\theta_A - 1)\exp[-(1/K_BT)V^{(2)}_A(Z_A)], \tag{8}$$

where $\delta(x)$ is the Dirac delta function and $V^{(2)}_A(Z_A)$ is the "smectic" part of the mean field, defining translational ordering along the z axis in our system. One-particle potentials $V^{(2)}_A(Z_A)(A = M, D)$ (i.e. distribution functions) should then be chosen of a form that allows the density waves of monomers and dimers in S_A phase to be described. De Jeu and Longa[10] regarded the period of these waves to be equal to the length of dimer d.

Such choice of a one-particle distribution function accounts for the existence of the S_A phase with a layer periodicity equal to the length of dimer d and allows the occurrence of the N_{re} phase under certain conditions to be explained. However, as was mentioned above, there are some compounds in which a subsequent temperature decrease gives rise to the appearance of a reentrant S_A phase (after the N_{re} phase) with the layer periodicity equal to the length of monomers l. This phase sequence cannot be described by the de Jeu and Longa theory since the choice of distribution functions used in their paper[10] excludes the existence of an S_A phase with the layer periodicity different to the length of dimer. In order to investigate the $N \rightarrow S_{A_1} \rightarrow N_{re} \rightarrow S_{A_{re}}$ phase sequence in the framework of the de Jeu and Longa model it is necessary to choose a one-particle potential $V^{(2)}_A(Z_A)$ ($A = M, D$) in a form that allows both an S_A phase with a layer periodicity equal to the length of the dimer d and one with the layer periodicity equal to the molecular length l to be described.

By analogy with McMillan's theory[11] and according to Eq. 6 this requirement can be satisfied using the following simple expressions:

$$\begin{aligned} V^{(2)}_M(Z_M) = {} & -(1 + X_D)^{-1}\{X_M V^{(1)}_{MM}\sigma^{(1)}_M \\ & + X_D V^{(2)}_{MD}\sigma^{(1)}_D)\cos(2\pi Z_M/d) + (X_M V^{(2)}_{MM}\sigma^{(2)}_M \\ & + X_D V^{(2)}_{MD}\sigma^{(2)}_D)\cos(2\pi Z_M/l), \end{aligned} \tag{9}$$

$$\begin{aligned} V^{(2)}_D(Z_D) = {} & -(1 + X_D)^{-1}\{(X_M V^{(1)}_{MD}\sigma^{(1)}_M \\ & + X_D V^{(1)}_{DD}\sigma^{(1)}_D)\cos(2\pi Z_D/d) + (X_M V^{(2)}_{MD}\sigma^{(2)}_M \\ & + X_D V^{(2)}_{DD}\sigma^{(2)}_D)\cos(2\pi Z_D/l)\}, \end{aligned} \tag{10}$$

where $V^{(1,2)}_{MM}$, $V^{(1,2)}_{MD}$, $V^{(1,2)}_{DD}$ are the constants defining the strength of interaction of the probe monomer with other monomers, probe dimer with monomers (or probe monomer with dimers) and probe dimer with other dimers, respectively, $\sigma^{(1)}_{M,D}$ and $\sigma^{(2)}_{M,D}$ are the smectic order parameters proportional to the amplitudes of the monomer and dimer density waves with a period equal to d and l, respectively. The case of $\sigma^{(1,2)}_{M,D} = 0$ corresponds to an N phase, if $\sigma^{(1)}_{M,D} \neq 0$, $\sigma^{(2)}_{M,D} = 0$ then our system is in an S_{A_1} phase with a layer periodicity equal to d, if $\sigma^{(1)}_{M,D} = 0, \sigma^{(2)}_{M,D} \neq 0$ then an S_{A_2} phase with a layer periodicity equal to l takes place and, finally, the case of$\sigma^{(1,2)}_{M,D} \neq 0$ corresponds to an S_A phase in which two density waves with periods equal to d and l, respectively, coexist.

If it is supposed (by analogy with McMillan's theory[11] that the order parameters $\sigma^{(1,2)}_{M,D}$ is given by

$$\sigma^{(1)}_A = \int \cos(2\pi Z_A/d) f_A \, d\vec{r}_A \, d\Omega_A \Big/ \int f_A \, d\vec{r}_A \, d\Omega_A \qquad (11)$$

$$\text{and} \quad \sigma^{(2)}_A = \int \cos(2\pi Z_A/l) f_A \, d\vec{r}_A \, d\Omega_A \Big/ \int f_A \, d\vec{r}_A \, d\Omega_A \qquad (12)$$

then we obtain the following expression for free energy F of our mixture of monomers and dimers:

$$\begin{aligned} F = F_N &+ (N/2)\{(X_M/(1 + X_D))^2 (V^{(1)}_{MM}\sigma^{(1)^2}_M + V^{(2)}_{MM}\sigma^{(2)^2}_M) \\ &+ 2(X_M X_D/(1 + X_D)^2)\,(V^{(1)}_{MD}\sigma^{(1)}_M\sigma^{(1)}_D + V^{(2)}_{MD}\sigma^{(2)}_M\sigma^{(2)}_D) \\ &+ (X_D/(1 + X_D))^2 (V^{(1)}_{DD}\sigma^{(1)^2}_D + V^{(2)}_{DD}\sigma^{(2)^2}_D)\} \\ &- (NK_BT/(1 + X_D))\{X_M \ln[(4\pi V)^{-1} \\ &\cdot \int d\Omega_M d\vec{r}_M \exp(-V^{(2)}_M/k_BT)] \\ &+ X_D \ln[(4\pi V)^{-1} \int d\Omega_D d\vec{r}_D \exp(-V^{(2)}_D|k_BT)]\}, \end{aligned} \qquad (13)$$

where F_N is the free energy of the mixture in the N phase.

It is easily seen, that both equations (11) and (12) can be obtained by minimization of the free energy (13). Furthermore, the integrand in (13) may be expanded in a series of $V_M^{(2)}/KT_B$ and $V_D^{(2)}/KT_B$ terms and one can express the free energy F as a power series in the order parameters $\sigma_{M,D}^{(1,2)}$.

There are two different cases: 1.) the dimer and monomer lengths are not commensurate ($l < d < 2\,l$) and 2.) these lengths are commensurate ($d = 2\,l$).

Let us consider the first case corresponding to LCs with a partially bilayer S_A phase in which reentrant behavior is observed.[4,5] Then our expansion is a series only of even powers of the parameters $\sigma_{M,D}^{(1,2)}$ and is given by:

$$
\begin{aligned}
F = F_N &+ (N/2)\{(X_M/(1 + X_D))^2(V_{MM}^{(1)}\sigma_M^{(1)^2} \\
&+ V_{MM}^{(2)}\sigma_M^{(2)^2}) + 2(X_M X_D/(1 + X_D)^2)\,(V_{MD}^{(1)}\sigma_M^{(1)}\sigma_D^{(1)} \\
&+ V_{MD}^{(2)}\sigma_M^{(2)}\sigma_D^{(2)}) + (X_D/(1 + X_D))^2(V_{DD}^{(1)}\sigma_D^{(1)^2} + V_{DD}^{(2)}\sigma_D^{(2)^2})\} \\
&- (Nk_BT/(1 + X_D))\{(X_M/4k_B^2T^2)(V_{MM}^{(1)^2}\sigma_1^2 \\
&\qquad + V_{MM}^{(2)^2}\sigma_3^2) + (X_D/4k_B^2T^2) \\
&\times (V_{MD}^{(1)^2}\sigma_2^2 + V_{MD}^{(2)^2}\sigma_4^2) - (X_M/64k_B^4T^4)(V_{MM}^{(1)^4}\sigma_1^4 + V_{MM}^{(2)^4}\sigma_3^4) \\
&- (X_D/64k_B^4T^4)(V_{MD}^{(1)^4}\sigma_2^4 + V_{MD}^{(2)^4}\sigma_4^4)\} \\
&+ \ldots\ldots \text{ terms of higher orders} \qquad (14)
\end{aligned}
$$

where
$$
\begin{aligned}
\sigma_1 &= (X_M\sigma_M^{(1)} + X_D(V_{MD}^{(1)}/V_{MM}^{(1)})\sigma_D^{(1)})/(1 + X_D), \\
\sigma_2 &= (X_M\sigma_M^{(1)} + X_D(V_{DD}^{(1)}/V_{MD}^{(1)})\sigma_D^{(1)})/(1 + X_D), \\
\sigma_3 &= (X_M\sigma_M^{(2)} + X_D(V_{MD}^{(2)}/V_{MM}^{(2)})\sigma_D^{(2)})/(1 + X_D), \\
\sigma_4 &= (X_M\sigma_M^{(2)} + X_D(V_{DD}^{(2)}/V_{MD}^{(2)})\sigma_D^{(2)})/(1 + X_D).
\end{aligned}
$$

Thus, the free energy of our system depends on four smectic order parameters and involves six constants $V_{MM}^{(1,2)}$, $V_{MD}^{(1,2)}$ and $V_{DD}^{(1,2)}$. In order to simplify further the analysis of expression (14) let us assume these constants satisfy the following relations:

$$(V^{(1)}_{MD}/V^{(1)}_{MM}) = (V^{(1)}_{DD}/V^{(1)}_{MD}) = \beta_1,\ (V^{(1)}_{DD}/V^{(1)}_{MM}) = \beta_1^2,$$

$$(V^{(2)}_{MD}/V^{(2)}_{MM}) = (V^{(2)}_{DD}/V^{(2)}_{MD}) = \beta_2,\ (V^{(2)}_{DD}/V^{(2)}_{MM}) = \beta_2^2,$$

Then $\sigma_1 = \sigma_2$, $\sigma_3 = \sigma_4$ and the expression (14) for free energy is given by

$$F = F_N + Nk_BT\{A_1\sigma_1^2 + A_2\sigma_3^2 + C_1\sigma_1^4 + C_2\sigma_3^4 + \ldots.\}, \tag{15}$$

where $A_1 = 1/2t^* - (X_M + \beta_1^2X_D)/(4t^{*2}(1 + X_D))$,

$$A_2 = \alpha/2t^* - \alpha^2(X_M + \beta_2^2X_D)/(4t^{*2}(1 + X_D)),$$

$$C_1 = (X_M + \beta_1^4X_D)/(64t^{*4}(1 + X_D)),$$

$$C_2 = \alpha^4(X_M + \beta_2^4X_D)/(64t^{*4}(1 + X_D)), \tag{16}$$

$t^* = K_BT/V^{(1)}_{MM}$ is the reduced temperature and $\alpha = V^{(2)}_{MM}/V^{(1)}_{MM}$.

As is well known, that such an expression describes a second order phase transition.

According to the general theory of this transitions[13] when $A_{1,2} > 0$ then $\sigma_1 = \sigma_3 = 0$, i.e. our system is in the N phase, the case $A_1 < 0$, $A_2 > 0$ corresponds to $\sigma_1 \neq 0$, $\sigma_3 = 0$, i.e. a S_{A_1} phase takes place, when $A_2 < 0$, $A_1 > 0$ then the S_{A_2} phase is observed, and finally the case $A_{1,2} < 0$ corresponds to $\sigma_{1,3} \neq 0$, i.e. both S_{A_1} and S_{A_2} phases coexist. From the dimer concentration X_D one can determine using (16) the reduced temperatures corresponding to each of these four cases, i.e. the phase diagram in the X_D, t^* plane can be drawn.

III. CONDITIONS FOR REENTRANT BEHAVIOR AND CHARACTERISTICS OF N → S_A AND S_A → N_{re} TRANSITIONS

Since the phase sequence, the temperatures and other characteristics of the phase transitions depend on the temperature dependence of the dimer concentration $X_D(t^*)$, on crossing the phase diagram it is necessary to determine this dependence.

Let us consider the process of dimer formation and decay. If it is supposed that the dimers are formed by the collisions of monomers, or in other words, the reaction M + M → D takes place, then the rate of this process is defined by

$$(\mathrm{d}N_D/\mathrm{d}t)_1 = K_1N_M^2 = K_1N^2(1 - X_D)^2/(1 + X_D)^2,$$

where K_1 is a certain temperature function. Further, if it is assumed, that the decay of the dimers is a result of their activation via collisions with other dimers and unpaired monomers, then the rate of decay is given by

$$\begin{aligned}(\mathrm{d}N_D/\mathrm{d}t)_2 &= -K_2N_MN_D - K_3N_D^2\\ &= -K_2N^2X_D(1 - X_D)/(1 + X_D)^2 - K_3N^2X_D^2/(1 + X_D)^2.\end{aligned}$$

Here K_2 and K_3 are temperature functions which may be represented as

$$K_{2,3} = K'_{2,3}\exp(-D/K_BT)$$

where D is now the dimer activation energy and $K'_{2,3}$ are weak temperature functions (in comparison with $\exp(-D/K_BT)$). *The equilibrium dimer concentration* X_D may be found from the condition of constancy (of the dimer number) at a fixed temperature, which is equivalent to the following equation:

$$K_1(1 - X_D)^2 - K_2(1 - X_D)X_D - K_3X_D^2 = 0, \qquad (17)$$

the solution of which is given by

$$X_D - \{[K_1/K_3 + (K_2/K_3)^2]^{1/2} - K_2/2K_3\}$$

$$\cdot\{1 + [K_1/K_3 + (K_2/2K_3)^2]^{1/2} - K_2/2K_3\}^{-1} \qquad (18)$$

Since K_1 and the ratio K'_2/K'_3 are weak temperature functions, the ratios K_1/K_3 and $K_2/2K_3$ can be assumed to be equal to $\alpha\exp(D/K_BT)$ and β, respectively, where α and β are constants ($\beta \sim 1$). Furthermore, if for simplicity β is assumed to be 1, then the temperature dependence of the dimer concentration $X_D(T)$ is defined by the following expression:

$$X_D = 1 - [\alpha\exp(D/K_BT) + 1]^{-1/2} \qquad (19)$$

The typical shape of the $X_D(T)$ curve is depicted in Figure 1 (curve 1).

Now we can investigate the conditions of the occurrence of the reentrant nematic phase. The temperature t_1^* of S_{A_1} phase appearance is determined by the crossing of $A_1(X_D, t^*) = 0$ and $X_D(t^*)$ curves in the X_D, t^* plane. A N_{re} phase can be observed if a second crossing of these curves is possible, at the temperature $t_2^* < t_1^*$, which is dependent on the shape of the $A_1 = 0$ curve, defined by (16). There are the two following cases:

1.) $\beta_1^2 \geqslant 2$. The typical shape of the curve $A_1 = 0$ corresponding to this value of the β_1^2 parameter is shown in Figure 1 (curve 2). It is easily seen, that in such a case the curves $A_1 = 0$ and $X_D(t^*)$ cannot cross twice and the appearance of a N_{re} phase is not possible.

2.) $\beta_1^2 < 2$. The typical shape of the curve $A_1 = 0$ corresponding to this value of β_1^2 is also depicted in Figure 1 (curve 3). It is seen, that in this case the second crossing of $A_1 = 0$ and $X_D(t^*)$ curves is possible (in principle), and one can expect the appearance of a N_{re} phase.

Let us consider the second case in detail and assume that $A_1 = 0$ and $X_D(t^*)$ curves are crossing in points $t_1^*(X_{D_1})$ and t_2^* (X_{D_2}), as

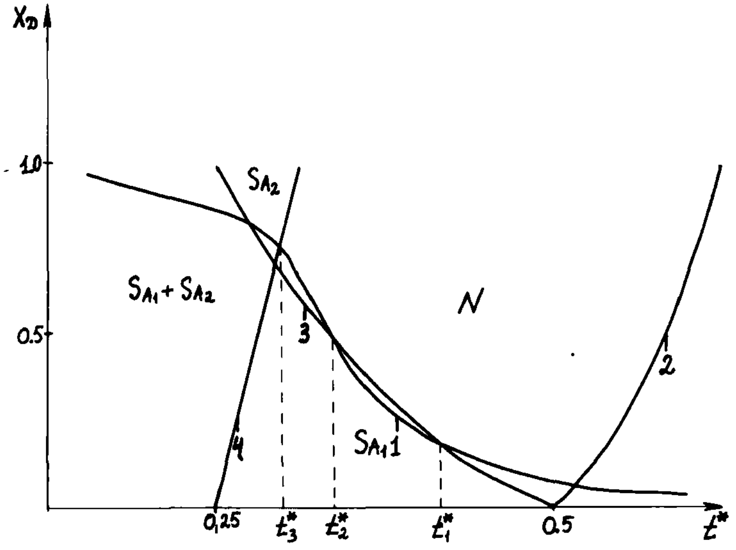

FIGURE 1 Phase diagram for mixtures of monomers and dimers and temperature dependence of the dimer concentration. 1.—$X_D(t^*)$ curve; 2.—$A_1 = 0$ curve for $\beta_1^2 \geqslant 2$; 3.—$A_1 = 0$ curve for $\beta_1^2 < 2$; 4.—$A_2 = 0$ curve.

shown in Figure 1. It is easily seen, that such double crossing is possible, if the slope of $X_D(t^*)$ curve is smaller than the slope of the $A_1 = 0$ curve at the $t_1^*(X_{D_1})$ point and conversely the slope of the former curve is larger than that of the latter curve at the $t_2^*(X_{D_2})$ point, i.e. $|(\mathrm{d}X_D/\mathrm{d}t^*)_2|_{t_1^*} < |(\mathrm{d}X_D/\mathrm{d}t^*)_1|_{t_1^*}$ and $|(\mathrm{d}X_D/\mathrm{d}t^*)_2|_{t_2^*} > |(\mathrm{d}X_D|\mathrm{d}t^*)_1|t_2^*$, where $(\mathrm{d}X_D/\mathrm{d}t^*)_1$ and $(\mathrm{d}X_D/\mathrm{d}t^*)_2$ define the slope angles of tangents to the $A_1 = 0$ and the $X_D(t^*)$ curves, respectively. Let us determine these slope angles.

According to (16) the equation $A_1 = 0$ is equivalent to the equation

$$t^* = [1 + (\beta_1^2 - 1)X_D]/2(1 + X_D) \tag{20}$$

the differentiation of which with respect to X_D gives

$$(\mathrm{d}X_D/\mathrm{d}t^*)_1 = 2(1 + X_D)^2/(\beta_1^2 - 2) \tag{21}$$

Also differentiating (19) with respect to temperature T, and taking into account that $\mathrm{d}X_D/\mathrm{d}t^* = \mathrm{d}X_D/\mathrm{d}T \cdot \mathrm{d}T/\mathrm{d}t^* = \mathrm{d}X_D/\mathrm{d}T \cdot V_{MM}^{(1)}/K_B$, one can obtain

$$(\mathrm{d}X_D/\mathrm{d}t^*)_2 = -(D/V_{MM}^{(1)})X_D(1 - X_D)(2 - X_D)/2t^{*2}.$$

At the points of crossing of the $A_1 = 0$ and $X_D(t^*)$ curves the reduced temperature t^* is determined by (20) which finally leads to

$$(\mathrm{d}X_D/\mathrm{d}t^*)_2 = -2(D/V_{MM}^{(1)})(1 + X_D)^2(1 - X_D)X_D \cdot (2 - X_D)[1 + (\beta_1^2 - 1)X_D]^{-2}. \tag{22}$$

Thus, the inequality $|(\mathrm{d}X_D/\mathrm{d}t^*)_2|_{t_1^*} < |(\mathrm{d}X_D/\mathrm{d}t^*)_1|_{t_1^*}$ for the $t_1^*(X_D)_1$ point is equivalent to

$$(2 - \beta_1^2)(D/V_{MM}^{(1)})X_{D1}(1 - X_{D1})(2 - X_{D1}) < [1 + (\beta_1^2 - 1)X_{D1}]^2 \tag{23}$$

and the reverse inequality for the $t_2^*(X_{D_2})$ point is equivalent to

$$(2 - \beta_1^2)(D/V_{MM}^{(1)})X_{D2}(1 - X_{D2})(2 - X_{D2}) > [1 + (\beta_1^2 - 1)X_{D2}]^2. \tag{24}$$

It is obvious, that there are always X_{D_1} values satisfying the former inequality, (23) whereas latter inequality (24) can only be satisfied under certain conditions, which are hence the conditions of appearance of the N_{re} phase.

For example, let us consider the case of $\beta_1^2 = 1$. Then inequality (24) turns into

$$(D/V_{MM}^{(1)})X_D(1 - X_D)(2 - X_D) > 1 \tag{25}$$

This inequality can be satisfied if

$$(D/V_{MM}^{(1)}) > [X_D(1 - X_D)(2 - X_D)]_{\max}^{-1} = \frac{(3)^{3/2}}{2}$$

Thus, we have obtained the relation between dimer activation energy D and the $V_{MM}^{(1)}$ constant which connect the reduced temperature t^* to the absolute temperature T, namely,

$$D/V_{MM}^{(1)} > \frac{(3)^{3/2}}{2}, \quad \text{or} \quad V_{MM}^{(1)} < 2D/(3)^{3/2}.$$

It is seen from Figure 1, that the reduced temperature t_1^* of the N → S_{A_1} transition is always < 1/2, i.e. $T_1 < V_{MM}^{(1)}/2K_B < D/(3)^{3/2}K_B$.

So, we can determine from the dimer activation energy D the upper boundary for the temperature interval of the existance of an S_{A_1} phase in liquid crystal compounds with a reentrant behaviour. The determination of the exact magnitude of the dimer activation energy (i.e. the energy of the coupling between two monomers forming a dimer) is a very complicated problem, because the LC molecules are macromolecules consisting of several tens of atoms. However, its magnitude can be approximately estimated (at least as to its order) from the following simple model.[14]

Let us represent the LC molecule as a spherocylinder (see Figure 2a) having a point polarizability centre and a point dipole moment situated on its long axis at distances a_{id} and a_d from the geometrical centre, respectively. Then the potential of interaction between these two molecules consists of three different parts:

1.) the potential of the dispersion forces

$$V_{id,id} = -(1/12)\bar{\alpha}^2 E r_{12}'^{-6}$$

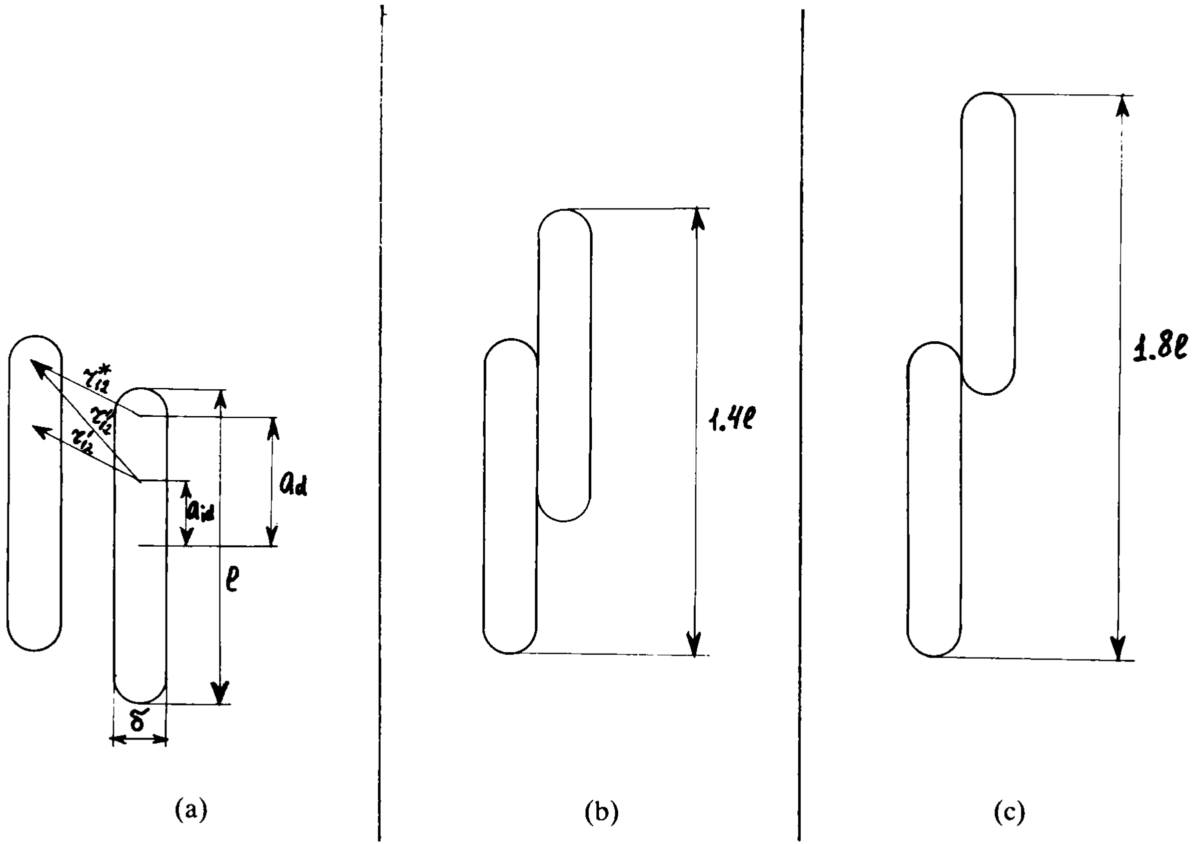

FIGURE 2 a.)—Liquid crystal molecules as hard spherocylinders; b.)—the dimer configuration for the partially bilayer S_A phase; c.)—the dimer configuration for the bilayer S_A phase.

where $\bar{\alpha}$ is the average polarizability of the molecules, E is the average energy of molecular activation, r'_{12} is the vector connecting the polarizability centres of the molecules;

2.) the potential of the induction forces

$$V_{d,id} = -(1/6)\bar{\alpha}\mu^2\{[1 + 3(\hat{a}_1\hat{r}''_{12})^2](r''_{12})^{-6} + [1 + 3(\hat{a}_2\hat{r}''_{21})^2](r''_{21})^{-6}\},$$

where μ is the permanent dipole moment of molecule aligned parallel to its long axis, $\hat{a}_1$ and $\hat{a}_2$ are the unit vectors defining the alignment of the long axes of the first and second molecules, respectively, r''_{12} (r''_{21}) is the vector connecting the dipole moment of the first (second) molecule to the polarizability centre of the second (first) molecule, $\hat{a}''_{12}$ and $\hat{a}''_{21}$ are the unit vectors parallel to these vectors;

3.) the potential of dipole-dipole interaction

$$V_{d,d} = \mu^2(r^*_{12})^{-3}\{(\hat{a}_1\hat{a}_2) - 3(\hat{a}_1\hat{r}^*_{12})(\hat{a}_2\hat{r}_{12}^*)\},$$

where r^*_{12} is the vector connecting dipole moments of the first and the second molecules.

Let us consider the pair of molecules forming the dimer and find the configuration of the pair which corresponds to the minimum of the interaction energy. This energy may be assumed to be the dimer activation energy. It is easy to show, that antiparallel orientation of the molecules is the most energetically favourable and if the maximum value of the dispersion energy $|V_{id,id}|$ is larger than that of the dipole-dipole interaction energy $|V_{dd}|$ then the dimer configuration depicted in Figure 2b ($d = 1.4\ l$) is more favourable than that depicted in Figure 2c ($d = 1.8\ l$). Conversely, if $|V_{dd}|_{\max} > |V_{id,id}|_{\max}$ the configuration in Figure 2c is more favourable than that in Figure 2b.

In order to estimate numerically the activation energy of the dimer depicted in Figure 2b the following values (typical for polar LC molecules) of the parameters have been used: $l = 30$ Å, $\delta = 5$ Å, $a_{id} = 0.21$, $a_d = 0.41$, $\bar{\alpha} = (40 \text{ to } 50)\ 10^{-24}\text{cm}^3$, $\mu = (4 \text{ to } 4.5)$D, $E = (e^2/r_0)$, $r_0 = 1$ Å. As a result of the estimation the dimer activation energy is found to be $D \approx (14 \text{ to } 18)\ 10^{-2}$ eV, which gives a quite reasonable value for the upper boundary of the temperature interval of existence of the S_{A_1} phase i.e. $T_1 < 390$ K (117°C). It is seen from

(24), that when $\beta_1^2 < 1$, we obtain a larger value for this upper boundary and for the case of $\beta_1^2 > 1$ corresponds to a lower boundary. Probably, the real situation corresponds to the case of $\beta_1^2 < 1$ (e.g. the S_{A_1} phase appears in the LC compound "T8" at 247°C (520 K)[6]).

Let us return to the phase diagram depicted in Figure 1. It is easily seen, that the $X_D(t^*)$ curve has to saturate after the second crossing with the $A_1 = 0$ curve and either at first crosses this curve again, or it crosses the $A_2 = 0$ curve. (curve 4 in Figure 1). In the first case the N_{re} phase is followed by a reentrant S_{A_1} phase with a layer periodicity equal to the length of dimer d. In the second case the new S_{A_2} phase with a layer periodicity equal to molecular length l appears after the N_{re} phase.

The experimental situation, observed up to now, corresponds to the second case,[3,6,7] but there are no reasons why the appearance of a reentrant S_{A_1} phase could not occur after the N_{re} phase. Also as can be seen from the phase diagram, further temperature decreases give rise to the transition of our system from an S_{A_2} phase to an S_A phase in which two density waves with periods equal to $d(l < d < 2l)$ and l, respectively, coexist. Probably this S_A phase was not observed hitherto because of the crystallization process beginning before its appearance. However it is possible that such S_A phases could be experimentally observed in some LC compounds with lower crystallization temperatures.

As mentioned above, from the expression (15) for the free energy of our system, it follows that in the framework of a saturated McMillan's theory the $N \rightarrow S_{A_1}$, $S_{A_1} \rightarrow N_{re}$ and $N_{re} \rightarrow S_{A_{re}}$ transitions are second order. It is well known that the first derivatives of free energy with respect to temperature are continuous at these transitions and the second derivatives such as the heat capacities C_p have discontinuities, which are given by:[13]

$$\begin{aligned}(\Delta C_p)_1 &= NK_BT_1^2(\partial A_1/\partial T_1)^2/2C_1,\\ (\Delta C_p)_2 &= -NK_BT_2^2(\partial A_1/\partial T_2)^2/2C_1,\\ (\Delta C_p)_3 &= NK_BT_3^2(\partial A_2/\partial T_3)^2/2C_2, \qquad (26)\end{aligned}$$

for the $N \rightarrow S_{A_1}$, $S_{A_1} \rightarrow N_{re}$ and $N_{re} \rightarrow S_{A_2}$ transitions, respectively. Let us calculate the heat capacity discontinuities $(\Delta C_p)_1$ and $(\Delta C_p)_2$. Taking into account, that $(\partial A_1/\partial T)^2 = (\partial A_1/\partial t^*)^2 k_B^2/V_{MM}^{(1)2} = (\partial A_1/$

$\partial t^*)^2 t^{*2}/T^2$ one can obtain

$$(\Delta C_p)_1 = Nk_B t_1^{*2}(\partial A_1/\partial t_1^*)^2/2C_1,$$

$$(\Delta C_p)_2 = -Nk_B t_2^{*2}(\partial A_1/\partial t_2^*)^2/2C_1.$$

Differentiating A_1 with respect to t^* and using the relation (20) for transition temperatures t_1^* and t_2^* one can obtain the following expression for the heat capacity discontinuities:

$$(\Delta C_p)_{1,2} = \pm 2Nk_B[1 + (\beta_1^2 - l)X_{D_{1,2}}]^2\{1 + (2 - \beta_1^2)(\mathrm{d}X_{D_{1,2}}/\mathrm{d}t^*)_2/2(1 + X_{D_{1,2}})^2\}\{(1 + X_{D_{1,2}})[1 + (\beta_1^4 - 1)X_{D_{1,2}}]\}, \tag{27}$$

where $X_{D_{1,2}}$ are the dimer concentrations at the N → S_{A_1} and S_{A_1} → N_{re} transition points and $(\mathrm{d}X_{D_{1,2}}/\mathrm{d}t^*)_2$ is the derivative of the temperature dependence of the dimer concentration at these points as given by (22).

For the concrete numerical computation let us consider the case $\beta_1^2 = 1$, in which the appearance of the N_{re} phase is possible when $(D/V_{MM}^{(1)}) > (3)^{3/2}/2 \approx 2.6$. Therefore we set $(D/V_{MM}^{(1)}) = 3$.

The values of dimer concentrations X_{D_1} and X_{D_2} corresponding to the points of the N → S_{A_1} and S_{A_1} → N_{re} transitions are determined from the inequalities (23) and (24), respectively, and for chosen parameters we obtain $X_{D_1} < 0.26$ and $0.26 < X_{D_2} < 0.61$.

For example, let us assume $X_{D_1} = 0.2$ and $X_{D_2} = 0.4$. Inserting these values into (22) and (27) one can obtain $(\Delta C_p)_1 = 0.03\ NK_B$ and $(\Delta C_p)_2 = 0.03\ Nk_B$, hence these discontinuities per one mole of substance are equal to 0.03 **R** and −0.03 **R**, respectively. In order to determine the heat capacity discontinuity $(\Delta C_p)_0$ given by the saturated McMillan's model for the classic LC it is necessary to insert $X_D = 0$ and $(\mathrm{d}X_D/\mathrm{d}t^*)_2 = 0$ into (27), which gives $(\Delta C_p)_0 = 2\ NK_B$, i.e. the heat capacity discontinuity per mole is equal to 2 **R**.

Thus, one can conclude, that in polar liquid crystals with reentrant behavior the heat capacity discontinuities associated with the N → S_{A_1} and S_{A_1} → N_{re} transitions are about one or two orders smaller than that associated with the second order N → S_A transition in a classical liquid crystal (i.e. when the orientational order is saturated).

It should be noted, that the calorimetric investigations of pure polar LC compound (8OCB) at high pressure[15] and the binary mixture (8OCB

+ 60CB) at atmospheric pressure[16] also revealed the considerable decrease of the heat capacity discontinuities associated with the N → S_A transitions in liquid crystals with reentrant polymorphism.

IV. APPLICABILITY OF THEORY TO THE DESCRIPTION OF THE $S_A \rightarrow S_{A'}$ TRANSITION

The expression (15) for the free energy of our system was obtained under the assumption of incommensurability of monomer and dimer lengths ($l < d < 2\,l$). One can show, that when these lengths are commensurate the expression for the free energy is given by

$$F = F_N + NK_BT\{A_1\sigma_1^2 + A_2\sigma_3^2 - G\sigma_1^2\sigma_3 + C_1\sigma_1^4 + C_2\sigma_3^4 \ldots \text{terms of higher order}\}, \quad (28)$$

where the $A_{1,2}$ and $C_{1,2}$ coefficients are the same as in (15) and G coefficient is given by

$$G = \alpha(X_M + \beta_1^2\beta_2X_D)/8t^{*3}(1 + X_D). \quad (29)$$

Expression (28) is analogous to that introduced phenomenologically by Meyer and Lubensky[17] for the description of the first order transition N → S_A in liquid crystals with a bilayer S_A phase.

Furthermore, it was shown by Prost,[18] that expressions of such a type predict the possibility of a direct $S_A \rightarrow S_{A'}$ transition. Thus, the proposed theory provides us with a description of this phenomenon at the microscopic level.

Detailed phase diagrams and the calculated characteristics of the N → S_A and $S_A \rightarrow S_{A'}$ transitions will be published elsewhere.

Acknowledgment

The author would like to thank Dr. V. N. Chirkov and Dr. L. S. Kogan for useful discussion of the present paper.

References

1. P. E. Cladis, *Phys. Rev. Lett.*, **35**, 48 (1975).
2. P. E. Cladis, R. K. Bogardus and D. Aadsen, *Phys. Rev.*, **A18**, 2292 (1978).
3. F. Hardouin, G. Sigand et al., *Phys. Lett.*, **71A**, 347 (1979).

4. A. J. Leadbetter, J. C. Frost et al., *J. Phys.*, **40**, 375 (1979).
5. F. Hardouin, A. M. Levelut and G. Sigaud, *J. Phys.*, **42**, 71 (1981).
6. F. Hardouin, G. Sigaud et al., *Solid State Commun.*, **30**, 265 (1979).
7. F. Hardouin and A. M. Levelut, *J. de Physique*, **41**, 41 (1980).
8. G. Sigaud, F. Hardouin et al., *J. de Physique, Colloq.*, **40**, C3–345 (1979).
9. F. Hardouin, A. M. Levelut et al., *Sol. State. Commun.*, **33**, 337 (1980).
10. L. Longa and W. de Jeu, *Phys. Rev.*, **A26**, 1632 (1982).
11. W. L. McMillan, *Phys. Rev.*, **A4**, 1238 (1971).
12. W. Maier and A. Saupe, *Z. Naturforsch.*, **13A**, 564 (1958); *ibid* **14A**, 882 (1959).
13. L. D. Landau and E. M. Lifshitz, "*Statistical Physics*" (Pergamon, London, 1968).
14. L. Longa and W. de Jeu, *Phys. Rev.*, **A28**, 2380 (1983).
15. C. W. Garland, G. B. Kasting and K. J. Lushington, *Phys. Rev. Lett.*, **43**, 1420 (1979).
16. K. J. Lushington, G. B. Kasting and C. W. Garland, *Phys. Rev.*, **22**, 2569 (1980).
17. R. B. Meyer and T. C. Lubensky, *Phys. Rev.*, **14A**, 2307 (1976).
18. J. Prost, *J. Phys.*, **40**, 581 (1979).