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A simple molecular model for N–SmA$_d$–N$_{dRe}$–N$_{1Re}$–SmA$_1$ phase sequence in highly polar compounds

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Our earlier model of re-entrant liquid crystalline phases exhibited by highly polar compounds, in which the mutual orientation of near-neighbour molecules can change from an antiparallel to a parallel configuration, has been extended to include both nematic and smectic interactions. We show that, as the McMillan parameter α is decreased, the SmA$_d$–SmA$_1$ line goes over to the SmA$_d$–N$_{1Re}$ line, finally becoming the N$_{dRe}$–N$_{1Re}$ transition line, the latter ending in a critical point. This sequence is in agreement with the predictions of Prost's Landau model as well as with an experimental result. The phase sequence N–SmA$_d$–N$_{dRe}$–N$_{1Re}$–SmA$_1$ is obtained on cooling for a range of α_A values.

1. Introduction

Liquid crystals composed of highly polar compounds exhibit double re-entrance and other unusual phenomena [1]. It is well known from the successful Landau theory of these phase transitions developed by Prost and co-workers [1–4], that the presence of two competing incommensurate lengths in the medium leads to these phenomena. We have proposed a simple molecular model [5] in which the molecular origin of the two lengths is explained as follows: the interaction between permanent dipoles favours an antiparallel orientation (A) between neighbouring molecules [6]. This interaction energy is $\propto 1/r^3$ where r is the intermolecular separation. The strongest intermolecular interaction arises from the anisotropic dispersion energy between the aromatic cores, resulting in the well known partial bilayer structure, figure 1(*a*). If the polar molecules are parallel, the dipolar interaction is repulsive. However, in view of the strong polarizability of the conjugated aromatic core to which the dipole is attached, the latter induces an oppositely oriented dipole moment in the neighbouring molecule, thus reducing the net dipole moment of each molecule, figure 1(*b*). Further, in this 'parallel' or (P) configuration, the chains are in close proximity, adding to the attractive interaction. Both these effects are $\propto 1/r^6$. Hence, as the density is increased, i.e. the temperature is lowered, one can expect a change in the configuration of the pairs from 'A'-type to 'P'-type. This implies the existence of a polar short range order at low temperatures. Indeed such a polar short range order has been experimentally detected very recently [7]. The two configurations shown in figure (1) account naturally for the two length scales in the Landau theory developed by Prost [2]. The McMillan parameter α which is a measure of the smectic interaction potential is larger for the 'A'-type of pairs compared with that for the 'P'-type of pairs, i.e. $\alpha_A > \alpha_P$ [5].

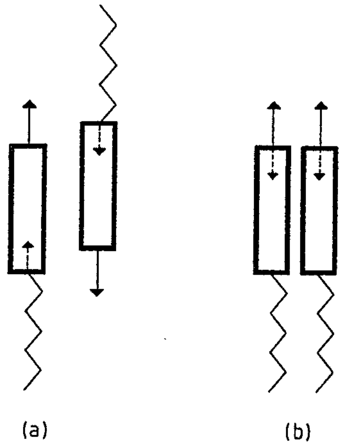

Figure 1. Schematic diagram showing (*a*) the antiparallel configuration of two molecules favoured at intermediate molecular separations, and (*b*) the parallel configuration favoured at relatively low values of intermolecular separation. Solid arrows represent permanent dipole moments and dotted arrows induced dipole moments. (For the sake of clarity, the relative separation in (a) is exaggerated.)

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We have developed a molecular theory of double reentrance using these ideas [5]. In a later paper [8], we extended the above model to predict the possibility of a first order nematic to nematic transition considering only the orientational interaction energy. Recent experiments indicate the possibility of such a nematic–nematic transition [7, 9]. In a recent paper [10], we have also extended this model to explain the SmA$_1$–SmA$_d$ transition assuming a saturated nematic order ($S=1$). Depending on the values of the parameters used, our calculations show the possibility of (i) a first order SmA$_1$–SmA$_d$ transition changing to a continuous SmA$_1$ to SmA$_d$ evolution beyond a critical point, (ii) a re-entrant nematic lake associated with the SmA$_1$–SmA$_d$ transition, and (iii) the re-entrant nematic lake merging with the nematic sea. Further, we have also used the model including both nematic and smectic interactions to explain our experimental studies on the effect of a strong electric field on some of these phase transitions [11].

The first example of a nematic–nematic transition was discovered in the re-entrant nematic range of a binary mixture [12], and was seen as a continuation of the SmA$_1$–SmA$_d$ transition line. This sequence was also predicted by the Landau theory [1]. In order to describe such a sequence, in the present short paper, we extend our model used in [10] to include both the nematic and smectic interactions. Our calculations show that, as the McMillan parameter α_A (and hence the chain length in a homologous series) is decreased, SmA$_d$–SmA$_1$ line goes over to the SmA$_d$–N$_{1\mathrm{Re}}$ line which finally becomes the N$_{d\mathrm{Re}}$–N$_{1\mathrm{Re}}$ transition line, the latter ending in a critical point, as seen in the experiment [12]. Also for a range of α_A values, we get the possibility of the N–SmA$_d$–N$_{d\mathrm{Re}}$–N$_{1\mathrm{Re}}$–SmA$_1$ phase sequence on cooling. Here, the suffix Re indicates that the nematic (N) is a re-entrant phase and the suffixes 'd' and '1' indicate that the short range (cybotactic) order of the polar molecules is of the 'partial bilayer' and 'monolayer' types respectively.

In the next section, the theoretical model is presented in brief. In § 3, the results of the calculation are discussed.

2. Theoretical model

2.1. *Assumptions*

In order to simplify the calculations, the following assumptions, which are discussed elsewhere in detail [5, 8], have been made.

(1) As described in the introduction, the medium is assumed to consist of 'pairs' of molecules having either antiparallel (A) or parallel (P) configurations.

(2) As we described earlier, the A-type (P-type) configuration is favoured at lower (higher) densities. For the sake of simplicity, it is assumed that the energy difference between the two configurations has the following form:

$$\Delta E = E_A - E_P = R_1 k_B T_{NI}\left(\frac{R_2}{T_R} - 1\right) \tag{1}$$

where k_B is the Boltzmann constant, E_A and E_P are the configurational energies of the A-type and P-type pairs respectively, T_{NI} is the nematic–isotropic transition temperature of the A-type pairs, $R_1 k_B T_{NI}$ is an interaction parameter and $T_R = T/T_{NI}$ is the reduced temperature. R_2 is the reduced temperature at which the density of the medium is such that ΔE becomes zero. For $T_R > R_2$, the A-type configuration has the lower energy.

(3) Since the A- and P-types of pairs are geometrically dissimilar, we assume the orientational potential for A-type pairs, U_{AA}, and P-type pairs, U_{PP}, to be different. We write, as in [8],

$$U_{PP} = YU_{AA} \tag{2}$$

and the mutual interaction potential

$$U_{AP} = U_{PA} = P(U_{AA}U_{PP})^{1/2} \tag{3}$$

where $P \neq 1$ indicates a deviation from the geometric mean (GM) rule in the orientational potential. The McMillan parameters for A-type (α_A) and P-type (α_P) configurations can be written as

$$\alpha_A = 2\exp\{-[\pi r_o/(r_o+2c)]^2\} \tag{4}$$

and

$$\alpha_P = 2\exp\{-[\pi r_o/(r_o+c)]^2\} \tag{5}$$

where r_o and c are the lengths of the aromatic and chain moieties of the molecule respectively. α_P is obviously related to α_A. The mutual interaction parameter

$$\alpha_{AP} = \alpha_{PA} = \alpha_E = Q(\alpha_A\alpha_P)^{1/2} \tag{6}$$

where $Q \neq 1$ indicates a deviation from the geometric mean rule in the smectic interaction.

(4) We decouple the translational and orientational parts in the McMillan's 'mixed' order parameter (σ) and as in [5] write

$$\langle P_2(\cos\theta)\cos(2\pi Z/d)\rangle = \langle P_2(\cos\theta)\rangle\langle\cos(2\pi Z/d)\rangle \tag{7}$$

i.e. $\sigma = S\tau$ where $\langle\ \rangle$ indicate a statistical average, $P_2(\cos\theta)$ is the second Legendre polynomial, θ the angle made by the molecular long axis with the director, Z the coordinate of the molecular centre along the direction of layer normal, d the layer thickness, and S and τ the nematic and the smectic order parameters, respectively.

(5) As explained in [10], a negative deviation from the geometric mean (GM) rule for the mutual interaction between the components can be expected (i.e. P and $Q < 1$) and also that the deviation increases as the molecular structures of the two components in a mixture become more dissimilar. Since P and Q always occur together in the terms representing the mutual interaction in all the equations, it is enough to consider such a deviation for P only. Hence, as explained in [10], we can write,

$$P = P^*(\alpha_A / \alpha_P) \tag{8}$$

where P^* is a constant chosen such that $P < 1$ in the entire series.

2.2. *Free energy and order parameters*

The medium is assumed to consist of a *mixture* of A-type pairs and P-type pairs. Extending the McMillan theory for mixtures, the potential energy of the ith A-type pair can be written as

$$\begin{aligned} U_{Ai} = & - U_{AA} X_A S_A P_2(\cos\theta_{Ai})[1 + \alpha_A \tau_A \cos(2\pi Z_i/d)_A] \\ & - U_{AP} X_P S_P P_2(\cos\theta_{Ai})[1 + \alpha_{AP} \tau_P \cos(2\pi Z_i/d)_A] \end{aligned} \tag{9}$$

where X_A, X_P, S_A, S_P and τ_A, τ_P are the mole-fractions, and orientational and translational order parameters of A- and P-type pairs respectively. Similarly for a P-type pair, U_{Pj} is obtained by interchanging suffixes A and P in equation (9). Now, the internal energy of one mole of pairs can be written as

$$2U = \frac{NX_A}{2}\langle U_{Ai}\rangle + \frac{NX_P}{2}\langle U_{Pj}\rangle - NX_P \Delta E \tag{10}$$

where the factor 2 on the left hand side reminds us that we have a mole of pairs and we have also added the concentration-dependent part of the configurational energy.

The molar entropy is given by

$$\begin{aligned} 2S = & - Nk_B\left[X_A \int f_{Ai} \ln f_{Ai}\, d(\cos\theta_{Ai})\, dZ_{Ai} \right. \\ & \left. + X_P \int f_{Pj} \ln f_{Pj}\, d(\cos\theta_{Pj})\, dZ_{Pj}\right] \\ & - Nk_B(X_A \ln X_A + X_P \ln X_P) \end{aligned} \tag{11}$$

where the last term is the entropy of mixing and f_A and f_P are the normalized distribution functions of A- and P-type pairs respectively. The Helmholtz free energy is given by:

$$F = U - TS. \tag{12}$$

The distribution functions f_A and f_P are found by minimizing F. We can show that the decoupling assumption (see equation 7), leads to the result

$$f_A = f_{Ao} f_{At}, \quad \text{and} \quad f_P = f_{Po} f_{Pt} \tag{13}$$

where f_{Ao} and f_{At} are the orientational and translational distribution functions of the A-type pairs and f_{Po} and f_{Pt} are similar functions for P-type pairs.

Hence the order parameters are given by:

$$S_A = \int_0^1 P_2(\cos\theta_{Ai}) f_{Ao}\, d(\cos\theta_{Ai}) \tag{14}$$

and

$$\tau_A = \int_0^1 \cos(\pi Z') f_{At}\, dZ' \tag{15}$$

where the reduced co-ordinate $Z' = (2Z_i/d)_A$ is used. S_P and τ_P are obtained by interchanging the suffixes A and P in equations (14) and (15). The equilibrium value of mole-fraction X_A of the A-type pairs is found by minimizing F with respect to X_A.

3. Results and discussion

We look for the following types of solution:

(1) $S_A, S_P \neq 0$, $\tau_A = \tau_P = 0$ leading to nematic phase which is N_1 if X_A is small and N_d if X_A is large;

(2) $S_A, S_P \neq 0$, $\tau_A, \tau_P \neq 0$ leading to the smectic phase which is SmA_1 if X_A is small and SmA_d if X_A is large.

For a given set of parameters, the free energy has four local minima w.r.t X_A, two corresponding to nematic phase and two to smectic phase. Of these, the phase corresponding to the absolute minimum is the stable one. Depending on which two of these four local minima are equal, we get the possibility of various phase transitions. As described earlier [8], the P-type configuration need not be confined to pairs and hence the effective orientational potential can be higher for P-type 'pairs' than for the A-type, i.e. $Y > 1$ in equation (2). We have shown in [8] that $P < 1$ leads to N_1–N_d transition and for a chosen set of Y, R_1 and R_2, there is a P_{critical} above which there is a continuous evolution between N_1 and N_d phases. We choose a value of P^* in equation (8) which gives $P < P_{\text{critical}}$ such that N_1–N_d transition is possible for the chosen values of Y, R_1 and R_2.

With $Y = 1.4$, $R_1 = 15$, $R_2 = 0.6$, $P^* = 0.15$ and $Q = 1$, we get the phase diagram shown in figure (2). The calculated phase diagram can be compared with that obtained by experiment in [12]. The experiment was made on a mixture of two compounds belonging to the same

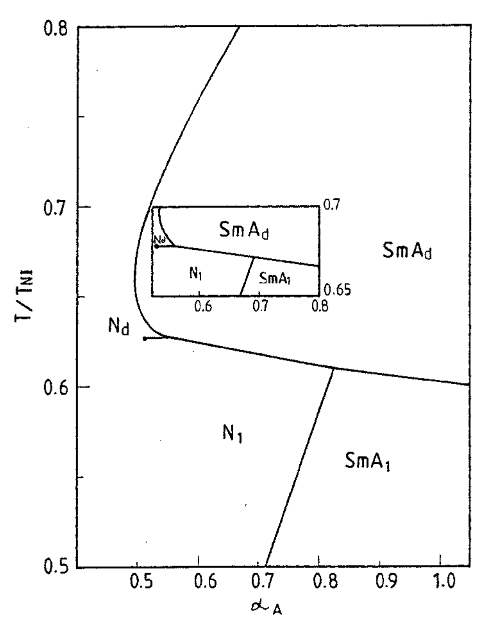

Figure 2. Calculated phase diagram with $R_1 = 15$, $R_2 = 0.6$, $P^* = 0.15$, $Y = 1.4$, $Q = 1$, showing the re-entrant N_d–N_1 (indicated in the text as N_{dRe}–N_{1Re}) transition line starting from a critical point; this continues as a SmA_d–N_1 line and extends as a SmA_d–SmA_1 line as α_A is increased. The inset is a similar diagram with P^* and Y increased to 0.18 and 2, respectively, showing that the SmA_d–N_1 transition occurs over a smaller range of α_A values.

homologous series, namely, DB_8ONO_2 and $DB_{10}ONO_2$. In the phase diagram, X denotes the mol % of the longer homologue $DB_{10}ONO_2$. Obviously, an increase in X is equivalent to increase in the McMillan parameter α. For example at $X = 53$, the SmA_d–N_{dRe}–N_{1Re}–SmA_1 sequence is seen on cooling. In our calculated phase diagram, for example, at $\alpha_A = 0.525$, we have the N–(0.7)–SmA_d–(0.63)–N_{dRe}–(0.627)–N_{1Re}–(0.323)–SmA_1 sequence on cooling (transition T_R values are indicated in parentheses; for the sake of clarity, the part of the phase diagram below $T_R = 0.5$ is not shown in the figure). On the lower α_A side, there is a re-entrant N_d–N_1 transition line which ends at a critical point (at $\alpha_A = 0.5123$ and $T_R = 0.6266$) and the line is seen over a range of α_A (0.5123 to 0.542). As α_A is increased above 0.542, the N_{dRe}–N_{1Re} transition line continues as a SmA_d–N_{1Re} line (for a range of $\alpha_A = 0.542$ to 0.83) and extends as a SmA_d–SmA_1 line (for $\alpha_A > 0.83$). These features agree with the experimental trends [12], in which there is a re-entrant N_d–N_1 transition line which ends at a critical point for lower values of X. For higher values of X, it extends to a SmA_d–N_{1Re} transition line and further to a SmA_d–SmA_1 transition line.

Keeping R_1, R_2, and Q the same, if Y and P^* are increased to 2 and 0.18, respectively, we get the similar phase diagram shown in the inset. In this case, the range of α_A exhibiting the SmA_d–N_{1Re} transition decreases. These diagrams are also similar to those predicted by the dislocation loop melting theory of Prost and Toner [4].

While the topology of the calculated phase diagram agrees with the experimental topology, the theory overestimates the temperature range of N_{1Re}. The molecular theory is necessarily over simplified, and a quantitative comparison is not possible. A more detailed theory of mixtures of polar compounds might give results in closer agreement with the experimental data.

In conclusion, our earlier molecular theory of smectic phases with saturated nematic order [10] has been extended to include nematic interactions and an appropriate deviation from the GM rule. It has been shown that as the McMillan parameter α_A (and hence the chain length in a homologous series) is decreased, the SmA_d–SmA_1 line goes over to the SmA_d–N_{1Re} line which finally becomes the N_{dRe}–N_{1Re} transition line, the latter ending in a critical point, as seen experimentally [12]. Also for a range of α_A, we get the possibility of N–SmA_d–N_{dRe}–N_{1Re}–SmA_1 phase sequence on cooling. The N_{dRe}–N_{1Re} transition occurs over a very small range of α_A.

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