An extension of the McMillan theory to a bilayer smectic A phase with long range antiferroelectric order

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Here an extension of the McMillan theory to describe both a monolayer smectic A phase with short range antiferroelectric order and a bilayer smectic A phase with long range antiferroelectric order in polar liquid crystals is proposed. In a molecular field approximation the single particle pseudopotential and self consistent equations which determine the usual orientational and translational order parameters and a new order parameter taking into account the antiferroelectric character of a bilayer smectic A structure are derived from a modified pair potential. The regions of existence for the isotropic, nematic, as well as both monolayer and bilayer smectic A phases together with the transitional characteristics are determined by numerical solution of the self consistent equations. In addition the temperature dependence of all the order parameters is determined. These results are compared with those from experiment.

1. Introduction

In addition to the nematic phase (N) and ordinary monolayer smectic-A phase (S_{A_1}) the bilayer smectic A phase (S_{A_2}) with a layer thickness, d, equal to nearly two molecular lengths $(d \approx 2l)$ exists in some strongly polar liquid crystals (DB5 or DB6) and their mixtures with non-polar mesogens [1–3]. In addition, direct transitions between monolayer and bilayer smectic A phases occurs in such liquid crystals.

A phenomenological description of the N–S_{A_2} and N–S_{A_1}–S_{A_2} phase transitions has been given by Prost [4]. Microscopic models for the S_{A_1} and S_{A_2} phases were proposed by de Jeu and Longa [5]. According to these models in the S_{A_1} phase the polar molecules form only a monolayer smectic A structure with short range anti-ferroelectric order (see figure 1 (a)) whereas in the S_{A_2} phase this monolayer structure coexists with a bilayer smectic A structure with long range antiferroelectric order (see figure 1 (b)). The model suggested by de Jeu and Longa is supported by dielectric studies [6] of the N–S_{A_1} and N–S_{A_2} transitions in the polar mesogens 4-n-alkylphenyl-4′-[4-cyanobenzoyloxy]benzoate (DB5 pentyl and DB6 hexyl) and their mixtures with the non-polar terephthalylidene-bis-(4-n-butylaniline) (TBBA) which revealed the anomalies inherent to the structures with antiferroelectric order. However in [5] it was assumed that the orientational order in the liquid crystal is perfect (i.e. the long axes of all the molecules are oriented parallel to the director **n**). Firstly such assumption is quite crude and secondly it does not allow us to compare the temperatures of the N–S_{A_2}, N–S_{A_1} and S_{A_1}–S_{A_2} transitions with liquid crystal the isotropic (I) transition temperature.

At present we have the well-known McMillan theory [7, 8] describing at the molecular level both orientational (nematic) and translational (smectic) ordering in
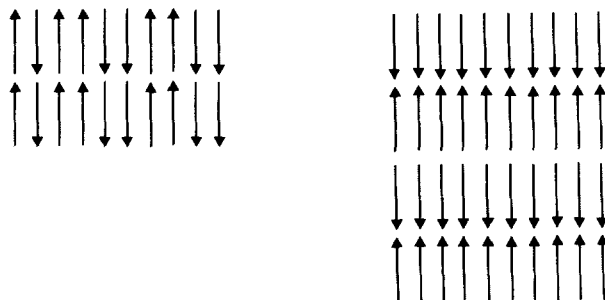
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Figure. 1. (a) Monolayer smectic A structure with short range antiferroelectric order.
            (b) Bilayer smectic A structure with long range antiferroelectric order.

the liquid crystal. However this theory is only suitable for the description of a monolayer smectic A phase consisting of completely symmetrical and non-polar molecules.

We propose here a simple extension of the McMillan theory to polar liquid crystals which allows to describe both a monolayer smectic A structure with short range antiferroelectric order (see figure 1 (a)) and a bilayer smectic A structure with long range antiferroelectric order (see figure 1 (b)). In the molecular field approximation the single particle pseudopotential is derived from a modified McMillan pair potential and, in addition, to the usual orientational and translational order parameters a new order parameter which takes into account the antiferroelectric character of the smectic A_2 structure is introduced. Numerical solution of the self consistent equations gives the regions of existence for the isotropic, nematic, smectic A_1 and smectic A_2 phases as well as the transitional characteristics and the temperature dependence of all of the order parameters is determined. The theoretical results are compared with experiment.

2. Microscopic description of monolayer and bilayer smectic A structures in a molecular field approximation

The McMillan theory (for simplicity we consider the original version [7]) is based on a model pair potential such that the two kinds of mutual molecular arrangement which correspond to the angle θ_{12} between the long molecular axis and the second with an angle $\theta_{12} + \pi$ are energetically equivalent. The single particle pseudopotential and consequently the single particle partition function derived from this pair potential are such that in any point of the liquid crystal the probability of molecular orientation parallel to the director ('up') equals to that of the antiparallel molecular orientation ('down'). It is certainly true for liquid crystals consisting of completely symmetric and non-polar molecules. However in polar liquid crystals consisting of asymmetric molecules having permanent electric dipole moment at one of molecular ends the complete equivalence of the parallel and antiparellel orientations ('up' and 'down') occurs in the isotropic, nematic and monolayer smectic A_1 phases but not in the S_{A_2} phase, in which in addition to the monolayer smectic A structure the bilayer smectic A structure with its long range antiferroelectric order exists (see figure 1 (b)). It is seen that each layer of this structure consists of two macroscopic sublayers with mutually opposite alignment of the molecular dipoles. In other words, if in the lower sublayer the preferential molecular orientation 'up' takes place then in next upper sublayer the preferential orientation 'down' occurs.

In order to describe, at the molecular level, both the monolayer smectic A structure with its short range antiferroelectric order (see figure 1 (*a*)) and the bilayer smectic A structure with its long range antiferroelectric order (see figure 1 (*b*)) we have to modify McMillan model pair potential [7] in such way as to break the equivalence (from an energetic point of view) of the two kinds of mutual arrangement of the molecules. It can be made in the simplest way by adding to the usual mcMillan potential a term proportional to $\cos\theta_{12}$. Thus we use the model pair potential

$$v_{12}(r_{12}, \theta_{12}) = - (v_0/Nr_0^3\pi^{3/12})\exp(-r_{12}^2/r_0^2)\,[(3\cos^2\theta_{12} - 1)/2 + \delta\cos\theta_{12}],$$
(1)

where v_0 is the interaction constant determining the nematic–isotropic transition temperature, r_{12} is the distance between molecular centres, r_0 is the characteristic distance for the molecular interaction, δ is a dimensionless parameter determining the strength of the additional molecular interaction breaking the symmetry between 'up' and 'down' molecular orientations in polar liquid crystals and N is the number of molecules.

In the molecular field approximation the state of any molecule is completely described by the single particle distribution function

$$f(\mathbf{r}_1, \theta_1) = \exp[- V_1(\mathbf{r}_1, \theta_1)/kT],$$
(2)

where $V_1(\mathbf{r}_1, \theta_1)$ is the single-particle molecular field pseudopotential given by

$$V_1(\mathbf{r}_1, \theta_1) = N \int dr_2 d(\cos\theta_2) V_{12}(r_{12}, \theta_{12}) f(\mathbf{r}_2, \theta_2) \bigg/ \int dr_2 d(\cos\theta_2) f(\mathbf{r}_2, \theta_2),$$
(3)

$\mathbf{r}_1$ is the coordinate of the molecular centre, and θ_1 is the polar angle between the long molecular axis and the director.

Since we want to describe both a monolayer smectic A structure with a period $d = l$ and a bilayer smectic A structure with a period $d = 2l$ then we must expand the pairwise potential (1) in a Fourier series with a characteristic period $2l$ along the z axis parallel to the director. Substituting the first three terms of this expansion into equation (3) and taking into account that the single particle distribution function describing the structures shown in figures 1 (*a*) and 1 (*b*) must satisfy the relation

$$f(z + l, \theta + \pi) = f(z, \theta)$$

we can obtain the expression for the single particle pseudopotential:

$$V(z, \theta) = -v_0[S(3\cos^2\theta - 1)/2 + \alpha\sigma\cos(2\pi z/l)(3\cos^2\theta - 1)/2$$
$$+ \beta P\cos(2\pi z/2l)\cos\theta],$$
(4)

where

$$\alpha = 2\exp\left[- \left(\frac{\pi r_0}{l}\right)^2\right], \quad \beta = 2\delta\exp\left[- \left(\frac{\pi r_0}{2l}\right)^2\right]$$

and S, σ and P are the order parameters defined by the self consistent equations

$$\left.\begin{array}{l} S = \langle(3\cos^2\theta - 1)/2\rangle, \\ \sigma = \langle\cos(2\pi z/l)(3\cos^2\theta - 1)/2\rangle, \\ P = \langle\cos(2\pi z/2l)\cos\theta\rangle, \end{array}\right\}$$
(5)

where

$$\langle A(z, \cos\theta)\rangle \;=\; \int dz d(\cos\theta) A(z, \cos\theta) f(\mathbf{r}, \theta) \Big/ \int dz d(\cos\theta) f(\mathbf{r}, \theta). \qquad (6)$$

Here S and σ are the well-known orientational and translational order parameters in the McMillan theory [7] and P is the new order parameter describing the bilayer antiferroelectric ordering of polar molecules. The free energy F and entropy S of the liquid crystal are determined by

$$(F/NkT) \;=\; (1/2t)(S^2 + \alpha\sigma^2 + \beta P^2) \;-\; \ln\!\left[(4l)^{-1} \int_0^{2l} dz \int_{-1}^{+1} d(\cos\theta) f(z, \theta) \right], (7)$$

$$(S/Nk) \;=\; -(1/t)(S^2 + \alpha\sigma^2 + \beta P^2) \;+\; \ln\!\left[(4l)^{-1} \int_0^{2l} dz \int_{-1}^{+1} d(\cos\theta) f(z, \theta) \right],$$

$$(8)$$

where $t = kT/v_0$ is the reduced temperature.

3. Numerical solution of the self consistent equations. Comparison with experiment

The self consistent equations (5) were solved numerically by an iteration method, and the solution minimizing the free energy at a given temperature was selected from all possible solutions corresponding to the isotropic phase ($S = \sigma = P = 0$), nematic phase ($S \neq 0, \sigma = P = 0$), smectic A, phase ($S \neq 0, \sigma \neq 0, P = 0$) and smectic A_2 phase ($S \neq 0, \sigma \neq 0, P \neq 0$). The transition temperature between any two phases was determined from the condition of equality of their free energies.
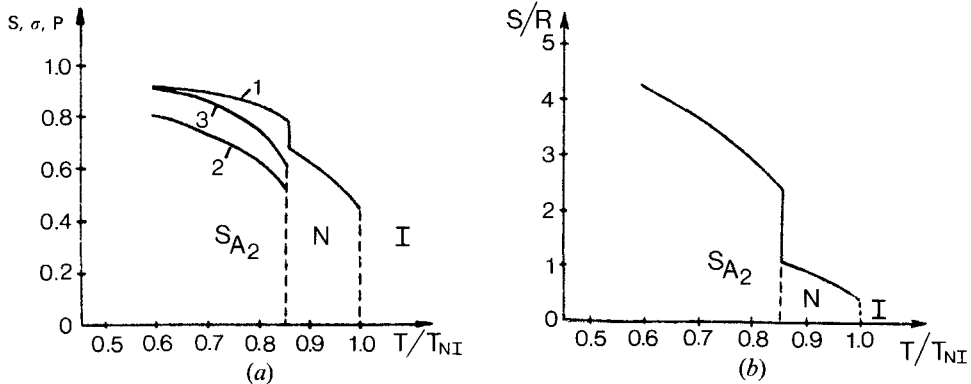

Figure 2. (a) Temperature dependence of the order parameters calculated with $\alpha = 0.65$, $\beta = 0.35$. $1 - S$, $2 - \sigma$, $3 - P$. (b) Temperature dependence of the entropy of polar liquid crystals at the same values of α and β.

The results obtained by numerical solution of equation (5) at three values of β (in all cases the α parameter was equal to 0·65) are shown in figures 2–4. Figures 2 (a) and (b) corespond to $\beta = 0.35$. It is seen that although the ratio of the S_{A_2}–N transition temperature to the N–I transition temperature ($T_{NS_{A_2}}/T_{IN}$) < 0·87 the S_{A_2} transition is first order. This result is in contradiction with the McMillan criterion according to which the S_A–N transition must be second order at (T_{NS_A}/T_{IN}) < 0·87 [7]. It should be noted that the S_{A_2}–N transition observed experimentally for polar liquid crystals. DB5 and DB6 are really first order transitions in contradiction with the McMillan criterion (for example in DB5 ($T_{NS_{A_2}}/T_{IN}$) = 0·79 [1]).
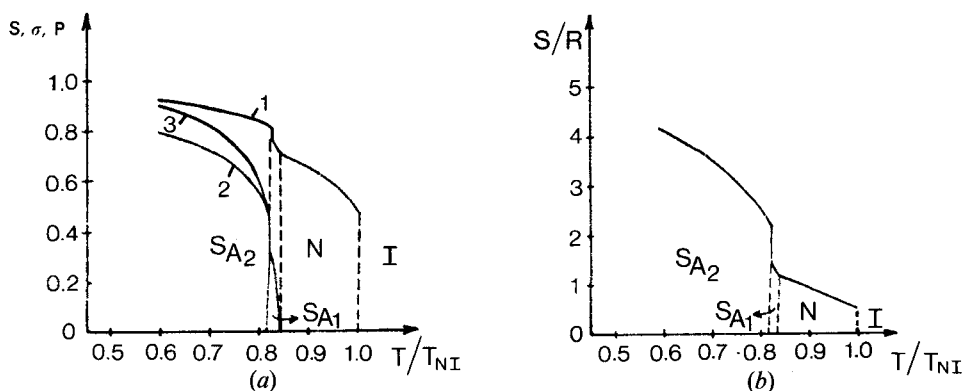
Figure 3. Temperature dependences similar to those in figures 2 (*a*) and calculated (*b*) with $\alpha = 0.65, \beta = 0.3$.
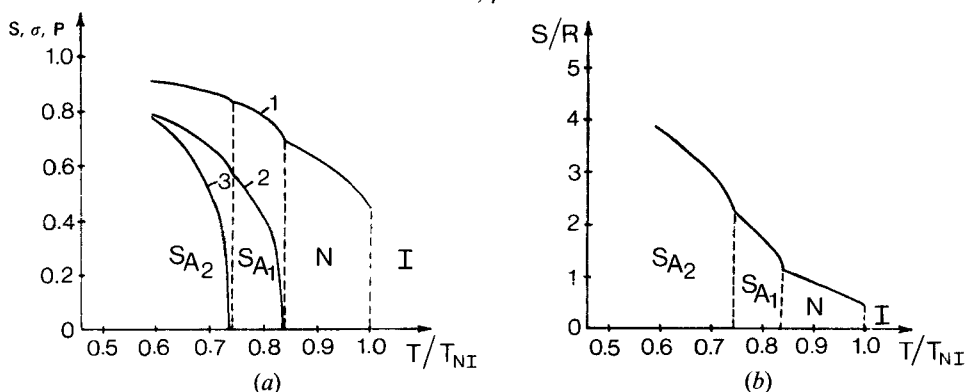

Figure 4. The temperature dependences of the order parameters (*a*) and entropy (*b*) found with $\alpha = 0.65, \beta = 0.22$.

Figures 3 (*a*) and (*b*) correspond to $\beta = 0.3$. It is seen that decreasing β and consequently the δ constant determining the strength of the part of the intermolecular interaction responsible for asymmetry between 'up' and 'down' orientations of polar molecules results in the replacement of the S_{A_2}–N first order transition (at $\beta = 0.35$) by the S_{A_2}–S_{A_1}–N phase sequence in which the S_{A_1}–N transition is second order and the S_{A_2}–S_{A_1} transition is first order. This result corresponds to the experimental situation for binary mixtures of polar liquid crystals (for example DB5) and non-polar mesogens (TBBA) [1–3]. When the concentration of the non-polar liquid crystal is smaller than a certain critical value x_0, then the first order transition S_{A_2}–N is observed in such mixtures. In the opposite case, when the concentration of the non-polar mesogen in the mixture is larger than x_0, the second order S_{A_1}–N transition takes place first and the first order transition between the monolayer S_{A_1} phase and the bilayer S_{A_2} phase is observed with further decreasing temperature. Probably the addition of non-polar and symmetrical molecules to a polar mesogen is equivalent to decreasing the interaction constant δ and consequently the parameter β.

Figures 4 (*a*) and (*b*) correspond to $\beta = 0.22$. It is seen that in this case the sequence of the S_{A_1}–N and S_{A_2}–S_{A_1} second order phase transitions takes place which is also observable in binary mixtures of polar and non-polar mesogens when the concentration of latter exceeds a certain value $x_1 > x_0$ [1].

Thus our theoretical results are in qualitative agreement with experiment. How-ever the theoretical values of the discontinuities in the entropy at the S_{A_2}–N and $S_{A_2-S_A}$ first order transitions are about 3–5 times larger than experiment [1]. Firstly the molecular field approximation always gives large entropy discontinuities at the phase transitions. Secondly, we proceeded from the model pairwise potential proposed by McMillan in his first paper [7] on the smectic A phase which gives a very large entropy discontinuity at the ordinary monolayer smectic A-nematic phase transition. Further McMillan proposed a somewhat modified expression for the pair potential and introduced an additional order parameter $\tau = \langle \cos(2\pi z/l) \rangle$ [8] which allowed him to obtain the value of entropy discontinuity at the S_A–N phase transition in accord with experiment

We can also carry out an analogous modification to our theory without any difficulty by simple addition of a certain constant δ_1 to the angular part of the pair potential (1). It is easily seen, that such modification does not lead to a major change in the results obtained and allows us to decrease the difference between theoretical and experimental values of the entropy discontinuities at the S_{A_2}–N and $S_{A_2}-S_{A_1}$ phase transitions.

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