



MEAN-FIELD MODEL FOR ANTIFERROELECTRIC SMECTIC-A LIQUID CRYSTALS

Lech Longa* and Wim H. de Jeu

Solid State Physics Laboratory, University of Groningen, Melkweg 1, 9718 EP Groningen, The Netherlands.

(received 7th March 1983 by P. Wachter)

A theoretical description is proposed for recently observed antiferroelectric smectic-A phases. Order parameters are introduced that retain information on the head-tail asymmetry of the constituent molecules and minimum ingredients are given for an averaged model potential. The calculations show that for high orientational order the antiferroelectric smectic-A structure is the best compromise between dipole repulsion and dispersive attraction. The resulting phase diagrams compare favorably with the experimental situation.

The nematic liquid crystalline phase is characterized by long-range orientational order of the constituent elongated molecules; they have their long axis, on average, parallel to a preferred direction in space. The classical picture of a smectic-A liquid crystal adds to that a density modulation parallel to the preferred direction, taken as the z-axis. Thus, a weak layer structure is observed with a periodicity $d \approx \ell$, where ℓ is the length of a molecule. Any possible asymmetry of the molecules is assumed to be nullified at a local molecular level (see Fig. 1a), an element which is retained in existing theoretical models.¹ Recently, evidence has become available that liquid crystals consisting of molecules with a strongly polar end group (CN or NO₂) give rise to a rather unexpected phase behavior.² Apart from the occurrence of a reentrant nematic phase, discussed earlier,³ additional smectic-A phases have been observed,⁴ some of which appear from their permittivities to have antiferroelectric character.⁵ It is the purpose of this communication to give a theoretical description of these new smectic-A phases, that is amenable to a microscopic interpretation.

The molecules under consideration possess polarizable centers like benzene rings as well as strong permanent dipole moments that are positioned near one end of a molecule, away from the geometrical center. Thus one can define head and tail of a molecule, and one could expect phases in which the up-down symmetry is broken, i.e. in which there is long-range ordering of heads and tails. *A priori* one expects two additional types of smectic-A phase with polarized layers⁶ (see Fig. 1). The S_{Af} phase (f for ferroelectric) carries an overall polarization. It has been discussed theoretically,⁷ but has not been observed so far. The S_{A2} phase has antiferroelectric character and a periodicity $d \approx 2\ell$. It has been observed experimentally^{2,4} and gives in X-ray investigations two sharp

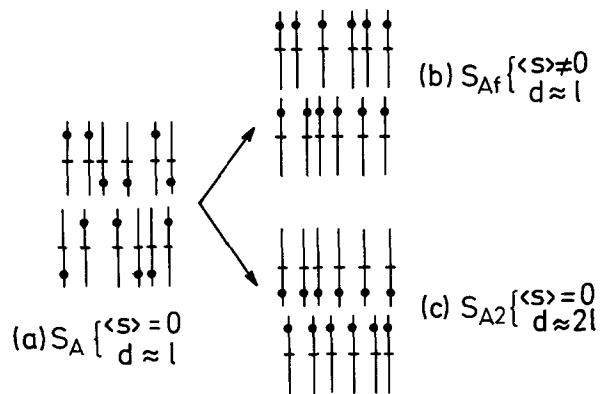


Figure 1 - Schematic representation for perfect orientational order and perfect layer structure of three possible types of smectic-A phases with asymmetric molecules: (a) "classical", (b) ferroelectric, (c) antiferroelectric.

Bragg-spots of approximately equal intensity at $d = \ell$ and $d = 2\ell$. Evidently, two density waves of different wave vector are present. With increasing temperature it may give way to the S_{A1} phase with one Bragg spot at $d = \ell$ and various types of diffuse spots at $d \approx 2\ell$. Sometimes there is an intermediate "antiphase" S_A. It is similar to S_{A1} or S_{A2}, but with an additional modulation in the xy-plane of a relatively large dimension. This aspect will not be included in the present discussion. The dielectric permittivity in both the S_{A1} and the S_{A2} phase is strongly reduced, indicating long-range antiferroelectricity. The permittivity in the S_{A2} phase is a smooth continuation of that of the S_{A1} phase.⁵

To define the model let us now consider a system of axially symmetric, spherocylindrical molecules that differ in head and tail. Additionally, we assume that the orientational order is ideal. Then the orientational degrees of freedom of a molecule can be described by one discrete

* Permanent address: Instytut Fizyki UJ, Reymonta 4, 30-059 Kraków, Poland.

pseudospin variable, $s = \pm 1$. It tells whether the head of a molecule points in the direction of the positive z -axis ("up", $s = +1$) or in the opposite direction ("down", $s = -1$). This approximation of ideal orientational order simplifies the numerical calculations considerably without affecting the qualitative conclusions from the model. The two-particle interaction will have a soft part and a part coming from the unpenetrable hard cores. Now, the problem is to approximate the soft part. As we want to describe antiferroelectric phases we emphasize (and idealize) the molecular asymmetry, and assume that each molecule possesses one polarizable center and one permanent dipole moment, located on the main axis of the spherocylinder at different distances away from the geometrical center. The molecular end where these interaction centers are situated will be taken as the head. Within the framework of such a model the attractive part of the interaction is composed of these parts:

- (i) Attractive induced dipole-induced dipole interactions;
- (ii) Attractive dipole-induced dipole interactions;
- (iii) Long-range dipole-dipole interactions.

Explicit formulas for these three types of interaction can be written down, and will be given in a future full paper. A full thermodynamic description of the system thus defined is still very complicated. However, some general trends, especially for the critical temperatures and for the order parameters, can be obtained from a calculation of the equilibrium properties within the mean-field approximation.

The next problem is the choice of the one-particle distribution function. For ideal orientational order it can be expected to depend only on z (the direction of the density wave) and on s . Hence we can write

$$P(z, s) = P_0(z) + s P_1(z). \quad (1)$$

The part $P_0(z)$ is responsible for "classical", non-polar smectic behaviour. It is the only part that survives for symmetric molecules. The part $P_1(z)$ is coupled to s and should lead to antiferroelectric phases. Note that antiferroelectricity is necessarily accompanied by long-range spatial order, and thus cannot be expected in the nematic phase. Hence, when antiferroelectric tendencies are strong, the part $P_1(z)$ alone might drive a transition to a smectic phase. From the experiments we know $P_0(z)$ to have a basic periodicity equal to d , while $P_1(z)$ has the double period. Keeping the lowest relevant orders in a Fourier expansion of $P_0(z)$ and $P_1(z)$ we get

$$P(z, s) = 1 + 2\tau \cos(2\pi z/d) + 2s \left[\frac{1}{2}\zeta_f + \zeta \cos(\pi z/d) + \zeta_1 \cos(2\pi z/d) \right] + \dots \quad (2)$$

The expansion coefficients are the order parameters, defined as

$$\begin{aligned} \tau &= \langle \cos(2\pi z/d) \rangle, \\ \zeta_f &= \langle s \rangle, \\ \zeta &= \langle s \cos(\pi z/d) \rangle, \\ \zeta_1 &= \langle s \cos(2\pi z/d) \rangle, \end{aligned} \quad (3)$$

where the brackets denote an average over $P(z, s)$. τ is the classical smectic spatial order parameter, while ζ and ζ_1 describe the double-layer and mono-layer tendency for polarized layers. ζ_1 must be retained because its spatial dependence is of the same order as that of τ . As both the S_{A1} and S_{A2} phase have antiferroelectric character, one anticipates that for the solutions corresponding to these phases the purely ferroelectric order parameter ζ_f vanishes. The choice of the reference point of the density modulation in the geometrical center of the molecules assures that no terms of the form $\sin(n\pi z/d)$ occur in Eq. (2).

Applying standard mean-field techniques to the potential described, and using Eq. (2) for the one-particle distribution function one arrives at the following set of selfconsistent equations:

$$\tau = Z^{-1} I(4, \cosh; \tau, \zeta_f, \zeta, \zeta_1), \quad (4a)$$

$$\zeta_f = Z^{-1} I(0, \sinh; \tau, \zeta_f, \zeta, \zeta_1), \quad (4b)$$

$$\zeta = Z^{-1} I(2, \sinh; \tau, \zeta_f, \zeta, \zeta_1), \quad (4c)$$

$$\zeta_1 = Z^{-1} I(4, \sinh; \tau, \zeta_f, \zeta, \zeta_1), \quad (4d)$$

$$Z = I(0, \cosh; \tau, \zeta_f, \zeta, \zeta_1), \quad (4e)$$

where $t = k_B T / (|w_1| \rho)$, k_B being Boltzmann's constant, T the absolute temperature and ρ the number density. Finally, the integral I is defined as

$$I(n, \text{func}; \tau, \zeta_f, \zeta, \zeta_1) = \int_0^1 dz \cos(n\pi z) \exp \left[\frac{b\tau \cos(4\pi z)}{t} \right] \text{func} \left[\frac{w_f \zeta_f + w\zeta \cos(2\pi z) + \text{sign}(w_1) \zeta_1 \cos(4\pi z)}{t} \right]. \quad (4f)$$

Among all solutions of Eqs. (4a-f) the physical one is the solution that minimizes the dimensionless free energy

$$G = \frac{1}{2} (b\tau^2 + w_f \zeta_f^2 + w\zeta^2 + \zeta_1^2) - t \ln Z. \quad (5)$$

The results depend on the three effective model parameters b , w_f and w , and on the scaled temperature t . These can be calculated directly from the interactions (i)-(iii) described above. They can also be interpreted as the partial energies of the system associated with the pure states described by τ , ζ_f and ζ , respectively, relative to that associated with ζ_1 . After some calculations one finds that w_f always has at least a weakly repulsive character: $w_f \gtrsim 0$. When the dipole moment is strongly terminal w dominates: $w > 1 > b \gtrsim 0$. When both the polarizable center and the dipole moment are close to the geometrical center one finds $b > 1 \gtrsim w \gtrsim 0$.

With some numerical effort, sets of order parameters $(\tau, \zeta_f, \zeta, \zeta_1)$ can be found from Eq. (4) that minimize the free energy. The repulsive character of the ferroelectric parameter w_f implies that no purely ferroelectric phase is predicted, and that of the 32 possible combinations of the four order parameters only 6 combinations can have physical significance. Two of the resulting phase diagrams are given in Figs. 2 and 3, calculated with $w_f = 0$. The solutions can be divided into four groups:

I Nematic: all spatial order parameters are zero.

II Classical smectic-A: $\tau \neq 0$.

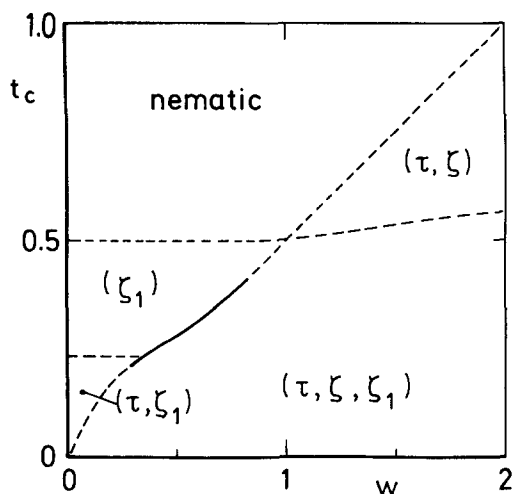


Figure 2 - Phase diagram in the case of a relatively small classical contribution to the stability of the smectic layer structure: $b = 0.3$. Full lines indicate a first-order transition, broken lines a second-order one.

III Antiferroelectric smectic-A:

- a) $\zeta_1 \neq 0$, smectic-A1,
 b) $\tau \neq 0$, $\zeta \neq 0$, smectic-A2.

IV Mixed ferroelectric/antiferroelectric smectic A:

- a) $\tau \neq 0$, $\zeta_1 \neq 0$, smectic-A1 like,
 b) $\tau \neq 0$, $\zeta \neq 0$, $\zeta_1 \neq 0$, smectic-A2 like.

Many of the phase transitions are predicted to be second-order, but under certain conditions first-order lines are found that terminate in multicritical points. This aspect will be discussed further elsewhere. The identification of the solutions I and II with experimentally observed phases is obvious. The two solutions III have the characteristics of the S_{A1} and S_{A2} phase, respectively: antiferroelectric symmetry, and for IIIb in addition two non-zero order parameters with different wave vectors. The transition to IIIa (S_{A1}) is driven by the antiferroelectric tendencies because $\tau = 0$. The non-zero ζ_1 can be interpreted as layers that have large polarized regions with different s , such that $\langle s \rangle = 0$.⁸ The occurrence of the solutions II and IIIa is mutually exclusive. At small values of w (dipole moment not strongly terminal and/or small) classical smectic-A behaviour is observed for $b > 1$, and a smectic-A1 phase for $b < 1$. This result might be important for our thinking about smectics with asymmetric molecules in general. Several phases of asymmetric substances simply classified as S_A could very well be of the antiferroelectric S_{A1} type.

Finally we come to the remaining solutions IV, that again have the characteristics of S_{A1} and S_{A2} , respectively. However, even for $w_f = 0$, due to a coupling between ζ_1 and τ in higher moments of the distribution function, a non-zero value of ζ_f is found. This should influence the permittivity of these phases, especially at temperatures away from the phase transition, where this ferroelectric effect could become important.

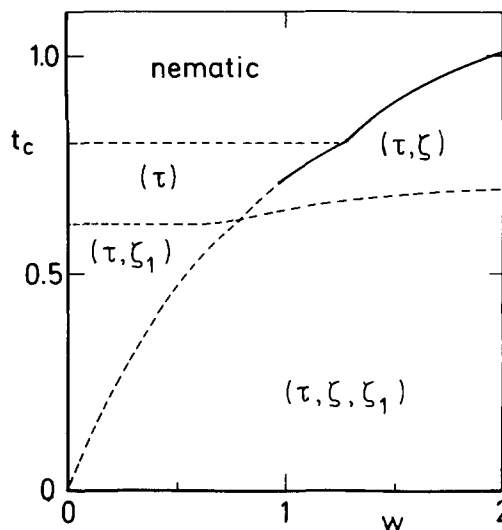


Figure 3 - Phase diagram for $b = 1.6$; as b and w now have the same order of magnitude the classical contribution to the smectic layers is relatively important. See further caption Fig. 2.

On the other hand, the prediction of a second S_{A1} phase (IVa) should probably not be taken too seriously, because in that situation the S_A^y phase interferes. In that phase there is a modulation in the xy -plane which is not present in our model. Inclusion of this aspect would modify the phase diagrams of Figs. 2 and 3, especially around the transition between the two S_{A1} phases. Also, inclusion of a non-zero w_f would change the phase diagrams such that the transitions to the phases IV are lowered. The other transitions are unaffected. Nevertheless, the prediction of two types of S_{A2} phase could be more realistic. The model indicates that an S_{A2} phase (IVb) below S_{A1} differs from one (IIIb) below N, which is accessible to experimental verification. The layer structure of IVb should be more pronounced due to the additional non-zero order parameter. This could show up as additional higher orders or more intense higher orders of the Bragg reflection corresponding to the layer spacing. There is no evidence for such an effect at this moment. However, a series of S_C phases exists: S_{Cd} , S_{C1} , S_{C2} , which are the tilted analogues of the S_A phases considered so far. Recently, two types of S_{C2} phase have been observed that differ in their Bragg reflections as described above.⁹ It would be very interesting to see whether they also differ dielectrically in the sense predicted by our model.

In conclusion we have given a model for antiferroelectric smectic-A phases. It differs from the Landau-type of theory by Prost,⁸ who emphasized incommensurability aspects. According to our model, for high orientational order, the phase transition nematic-smectic can be driven by the antiferroelectric forces, which gives the best compromise between the repulsion of the permanent dipole moments and the attractive induced interactions. This result might be relevant for smectic phases of asymmetric molecules in general, even in the absence of strong terminal dipoles.

REFERENCES

1. (a) K.K. Kobayashi, *J. Phys. Soc. Japan* 29, 101 (1970); (b) W.L. McMillan, *Phys. Rev. A* 4, 1238 (1971).
2. For a review see: F. Hardouin, A.M. Levelut, G. Sigaud, M.F. Achard, Nguyen Huu Tinh, and H. Gasparoux, *Symmetries and Broken Symmetries*, edited by N. Bocarra (Proc. Int. Coll. Pierre Curie, 1981), p. 231.
3. (a) W.H. de Jeu, *Solid State Commun.* 41, 529 (1982); (b) L. Longa and W.H. de Jeu, *Phys. Rev. A* 26, 1632 (1982).
4. A.M. Levelut, R.J. Tarento, F. Hardouin, M.F. Achard, and G. Sigaud, *Phys. Rev. A* 24, 2180 (1981), and references therein.
5. (a) L. Benguigui and F. Hardouin, *J. Phys. Lett.* 42, L-111 (1981); (b) *ibid* 42, L-381 (1981).
6. A. Saupe, *Mol. Cryst. Liq. Cryst.* 7, 59 (1969).
7. (a) P.J. Photinos and A. Saupe, *Phys. Rev. A* 13, 1926 (1976); (b) A. Michelson, D. Cabib and L. Benguigui, *J. Phys.* 38, 961 (1977).
8. J. Prost, *Liquid Crystals of One- and Two-Dimensional Order*, edited by W. Helfrich and G. Heppke (Springer, Berlin, 1980), p. 125.
9. F. Hardouin, Nguyen Huu Tinh, and A.M. Levelut, *J. Phys. Lett.* 43, L1-779 (1982).