

ON THE MOLECULAR THEORY OF SMECTIC-A LIQUID CRYSTALS

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Abstract The intermolecular interactions leading to the various types of smectic-A phase are considered both for effectively symmetric and for asymmetric molecules. At least a qualitative understanding of the molecular organization in the various phases can be obtained by combining the tendency of aromatic and aliphatic parts to segregate with optimal packing and minimal dipolar repulsions. In particular, it is shown that probably two rather different ways of molecular ordering may lead to a smectic-A phase with a period approximately equal to the molecular length.

1. INTRODUCTION TO SMECTIC-A PHASES

In this paper I propose to review what I believe to be the present state of our understanding at the molecular level of the various types of smectic-A phases that have been observed. I will do so in an informal way, trying to emphasize the basic ingredients and the results of the various models, rather than going into the formal details.

Figure 1 shows the textbook picture of a nematic (N) and a smectic-A ( $S_A$ ) phase of rodlike molecules. The molecules are, on the average, aligned with their long axis parallel to a certain direction in space (taken as the z-direction). In the following this orientational order will be considered to be a constant background and occasionally assumed to be perfect. The smectic phase is distinguished from the nematic one by a density modulation along the z-axis. This leads to what has loosely been called:

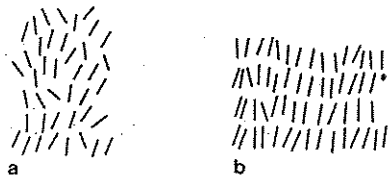


Fig. 1. Nematic (a) and smectic-A phase (b).

a structure of stacked liquid layers. However, it should be emphasized that the density modulation is very weak, contrary to the suggestion implied by the word layer. Indicating the repeat distance by  $d$ , the density wave can be described by a Fourier-series [1,2]:

$$\rho = \sum \rho_n \cos(2\pi n z/d) \quad (1)$$

where the  $\rho_n = \langle \cos(2\pi n z/d) \rangle$  are the smectic order parameters, the brackets indicating the average over the distribution function. Series (1) can be truncated after one term, leading to

$$\tau = \rho_1 = \langle \cos(2\pi z/d) \rangle, \quad (2)$$

which is called the smectic order parameter. In the simplest case  $d$  is taken equal to  $\ell$ , the length of the molecules.

Essential to simple molecular models of the smectic-A phase is the combination of Eq. (2), which contains the layer-spacing  $d \approx \ell$ , with a second length. The most important aspect is the division of the molecule into an aromatic and an aliphatic part (Fig. 2). Without paying attention to the actual interaction mechanisms I mention the well-known fact that these parts have a tendency to avoid each other and prefer like ones as neighbors. Thus it can be expected that the interaction energy of two molecules of the type pictured in Fig. 2 is minimal in a smectic-like configuration with the aromatic centers in equidistant planes. Working-out such models the smectic phase is, as expected, found to be stabilized for small enough values of  $r_0/\ell$ . Of course, to make these ideas quantitative, the details of the particular model must be considered [3]. The resulting behavior is qualitatively in reasonable agreement with the phase-behavior of many homologous series. In these series  $r_0$  can be taken as approximately constant and  $\ell$  as variable.

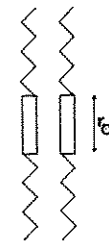


Fig. 2. Schematic representation of two molecules in a smectic-like configuration.

For the present purpose it is important to note that for many systems  $d$  as measured by X-ray diffraction is indeed approximately equal to  $\ell$ . Furthermore, the absence or weakness of higher-order reflections indicates that Eq. 2 is a good approximation. Centro-symmetric molecules as pictured in Fig. 2 are rare, but the same type of argument can be applied to other series, provided there is on a local level an equal distribution of molecules pointing "up" (positive  $z$ -direction) or "down." This also implies that in a first approximation permanent dipole moments play, at most, a minor role. These extensions of the original argument are justified because the phase behavior of many homologous series of non-symmetric molecules (which thus necessarily have dipole moments) is very similar to that of the few series with symmetric molecules [4].

## 2. ASYMMETRIC MOLECULES, THE $S_{Ad}$ -PHASE, AND REENRANT NEMATIC BEHAVIOR

Now I will consider the extreme case of an asymmetric molecule, one with an aromatic head and just one aliphatic tail. Evidently the type of argument of the previous section cannot be extended directly. The combination of a smectic density modulation with period  $d \approx \ell$  and a random up-down distribution will certainly not promote an optimum neighborhood for the aromatic and aliphatic parts. Assuming that these parts still prefer to segregate, clearly two solutions are possible, shown in Fig. 3. These two configurations each have their own specific problems:

- Situation I provides an unfavorable packing with crowded aromatic regions and open space around the aliphatic parts. From the packing point of view case II will be favored.
- In general, dipoles will be present in asymmetric molecules. As far as the component along the long molecular axis is considered, in case II dipolar repulsions will occur. From the dipolar point of view situation I will be favored.

From these observations one is tempted to conclude that under the appropriate conditions each of the two situations might be observed. This is

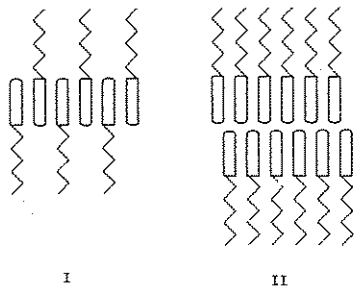


Fig. 3. Idealized sketch of the two possibilities for segregation of aromatic and aliphatic parts of asymmetric molecules.

indeed the case. In the remaining part of this section I will discuss case I, which in principle leads to the  $S_{Ad}$  phase. A discussion of the so-called  $S_{A2}$  phase that results from situation II will be postponed until the next section.

Any molecular model of the  $S_{Ad}$  phase should account for the following observations:

- (1) For the layer spacing  $d$  one finds  $l < d < 2l$ . If the aromatic and aliphatic parts have length  $a$  and  $b$ , respectively, one finds for several compounds approximately [5]:

$$d \approx a + 2b \quad (3)$$

There is no universal trend for the temperature dependence of  $d$ . In many cases temperature variations are minor, but both increases and decreases have also been observed.

- (2) Apart from the phase-transition  $NS_{Ad}$  often also a transition  $S_{Ad}^N$  reentrant (reentrant nematic) occurs.
- (3) In high-resolution studies of the phase transitions no difference is found between the critical behavior of the "classical"  $NS_A$  transition and the  $NS_{Ad}$  transition [6]. Here "classical" stands for the effectively symmetric case discussed in section 1.
- (4) The  $S_{Ad}$  phase usually occurs in compounds with a strongly polar end group at the end of the aromatic part, such as  $-CN$  or  $-NO_2$ . The average dielectric permittivity is given by

$$\bar{\epsilon} \sim \frac{\mu_{eff}^2}{3k_B T} \approx \frac{1}{2} \frac{\mu_{free}^2}{3k_B T} \quad (4)$$

indicating a considerable amount of anti-parallel dipole correlation. Most importantly this behavior is not only found in the  $S_{Ad}$  phase, but also in the nematic and the isotropic phase occurring at higher temperatures [7].

Some years ago Longa and I formulated a dimer model for the  $S_{Ad}$  phase [8]. Guided by Eq. 3 and similar observations by Cladis [9], it was assumed that the dipolar and other interactions between the compounds involved would lead to a dynamic monomer-dimer equilibrium



For the purpose of a model calculation the monomers and dimers were represented by the bodies pictured in Fig. 4. In this way the basic mechanism discussed in section 1 can still be effective. The monomer has no intention of supporting a smectic density wave, but the dimers are symmetric again, and will do so for small enough values of  $r_0/d'$  (where now  $d'$  is the length of the dimer). In addition to this requirement there must be, of course, a sufficient number of dimers, which makes the phase transition  $NS_{Ad}$  percolation like. Hence it is again the tendency of aromatic and aliphatic parts to segregate (but this is only possible for the dimers) which causes the smectic density wave. In the model of Fig. 4 the free energy describing the system contains in addition to the rotational entropy  $S_r$ , an extra packing entropy  $S_p$ :

$$F = U - TS_r - TS_p \quad (6)$$

Once the  $S_{Ad}$  phase has been established, with decreasing temperature or increasing pressure (increasing dimer concentration and/or increasing smectic order parameter) this term becomes increasingly important due to the central slightly bulkier part of the dimers. Because of the unfavorable packing entropy, dimers then have to move out of the smectic planes. Finally this destabilizes the smectic phase, leading to reentrant nematic behavior.

Several comments can be made concerning this type of model:

- Once Eq. 5 is accepted, in practice all the experimental observations follow in a natural way, in particular also the equivalence of the "classical"  $NS_A$  and the  $NS_{Ad}$  transition.
- The driving force for reentrant nematic behavior is the packing entropy. Hence, one can imagine that other mechanisms leading to such a term could give similar effects. Dowell has emphasized the importance of the temperature dependence of the conformation of the alkyl chains [10]. Provided the right packing entropy evolves, thus also reentrant nematic behavior is possible with non-polar molecules.

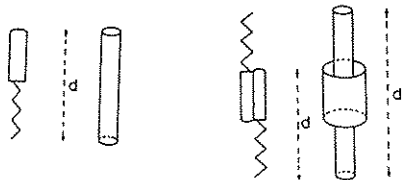


Fig. 4. Monomer and dimer with their model representation.

- The definition of the dimer and the underlying forces is not very precise. It is quite feasible that several types of dimers are possible with a somewhat different overlap, in particular if this promotes a favorable conformation and packing of the alkyl chain. Incorporation of such a possibility into the model would probably lead to multiple reentrant behavior with various nematic regions separated by  $S_{Ad}$  phases with different periodicities.
- The position of the dipole moment within the aromatic part of the molecule is rather unimportant, the most favorable situation being obtained with strongly conjugated dipoles. This contrasts with the situation to be discussed in the next section.
- One might wonder whether n-mers with  $n > 2$  should be taken into account as well. In particular, Berker ascribed the stability of the  $S_{Ad}$  phase to the existence of a two-dimensional network of antiparallel molecules in a background of n-mers of which many with  $n = 2$  [11]. Though one might question whether such a structure is compatible with the liquid nature of the  $S_{Ad}$  layers, it is interesting to note that this mechanism and the dimer-model are not mutually exclusive. Whether one of the two is dominant could probably be inferred from a more full calculation of the interaction energy of the molecules. I conclude that in spite of the objections that can and have been made against the dimer-model, it still seems to provide the only rather complete microscopic account of the present experimental situation.

### 3. ANTIFERRO-ELECTRIC SMETIC-A PHASES

In this section I will discuss possibility II for aromatic and aliphatic molecular parts to segregate as mentioned at the beginning of the previous section (see Fig. 3). As this leads to ferro-electric layers, the succession of neighboring layers must be considered. This succession can evidently be parallel (leading to macroscopic ferro-electricity,  $S_{Af}$  phase) or anti-parallel (leading to longrange antiferro-electricity and

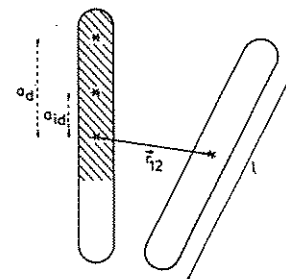


Fig. 5. Molecular model for calculating the interactions in asymmetric molecules; a dipole moment and a polarizable center are situated at  $a_d$  and  $a_{id}$  from the molecule center, respectively.

bilayer periodicity,  $S_{A2}$  phase). The important molecular interactions have been calculated by Longa and De Jeu using the molecular model of Fig. 5 [12]. The results for the dipolar repulsions are displayed in Fig. 6. As is to be expected, the  $S_{Af}$  phase is strongly destabilized, in agreement with the fact that it has not been observed experimentally. More interestingly, the dipolar repulsions become quite small in the antiferro-electric  $S_{A2}$  phase, provided the dipoles are localized at the end of the molecules. This is due to the favorable contribution of the interaction between the dipoles in the neighboring layers. In combination with the optimal packing this causes the  $S_{A2}$  phase to be the lowest temperature smectic-A phase, as observed experimentally. In a truncated Fourier-

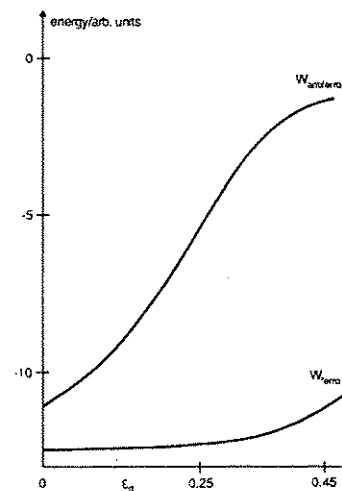


Fig. 6. Dipole repulsions for the  $S_{Af}$  and  $S_{A2}$  phase as a function of the dipole position  $\epsilon_d = a_d/l$  along the axis.

expansion analogous to Eqs. 1 and 2 the  $S_{A2}$  phase can be described by an order parameter

$$\xi = \langle s \cos(\pi z/d) \rangle, \quad (7)$$

where  $s = +1$  or  $-1$  indicates whether the polar head is respectively up or down. In agreement with this model, the dielectric permittivity in the  $S_{A2}$  phase is observed to be strongly reduced compared with the nematic phase at higher temperature [13]. This provides direct evidence for the long-range antiferro-electricity.

The situation is experimentally more complex than described so far. In the case of asymmetric molecules with strongly polar end groups such as  $-\text{CN}$  and  $\text{NO}_2$ , several more types of  $S_A$  phase have been observed. It will be clear from the discussion so far that a competition can exist between the tendency to condense as  $S_{Ad}$  or as  $S_{A2}$ . As the two wavelengths involved have no direct relation, this could in principle lead to an incommensurate smectic-A phase as predicted by Prost et al. [14]. Such a phase, characterized by two sharp X-ray reflections at incommensurate values, has recently been observed [15]. It seems that this type of phase is rare. A probable explanation is that the (in)commensurability problem can be solved in a different way, that being by imposing a modulation upon the  $S_{A2}$  structure as pictured in Fig. 7. X-ray results for this so-called  $S_{\tilde{A}}$  phase indicate that the modulation varies from "walls" at lower temperatures to a more sinusoidal modulation at higher temperatures. It seems that this additional modulation is one-dimensional, thus introducing a unique direction within the smectic planes [16]. This makes the  $S_{\tilde{A}}$  phase biaxial, quite different from the phases discussed so far, and the name Smectic A not very proper.

I cannot infer any mechanism for the asymmetric molecules discussed so far to condense as a "classical"  $S_A$  phase with  $d \approx \ell$  and a random up-down distribution of the molecules. Such a situation would completely counteract a segregation of aliphatic and aromatic parts, and probably even enhance the free energy compared with the nematic phase. Nevertheless,  $S_A$  phases with  $d \approx \ell$  have been observed with asymmetric molecules with terminal  $-\text{CN}$  or  $\text{NO}_2$  groups, often below a reentrant nematic phase. They have sometimes been named  $S_{A1}$ , to emphasize  $d \approx \ell$ , and to distinguish them from the  $S_{\tilde{A}}$  and  $S_{A2}$  phases that usually occur in the same region of the phase diagram at lower temperatures. The molecular theory of Longa and de Jeu

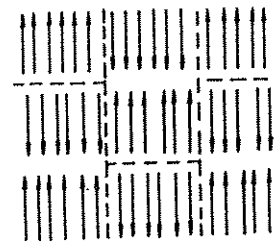


Fig. 7. Schematic structure of the  $S_{\tilde{A}}$  phase.

allows for such a phase, characterized by an order parameter

$$\zeta_1 = \langle s \cos(2\pi z/d) \rangle \quad (8a)$$

with in addition

$$\tau = \zeta = 0 \quad (8b)$$

The only way to accommodate this combination of order parameters is a superposition of two ferro-electric stacks of layers that are antiparallel and shifted over  $d/2$ . There is no evidence that this corresponds to the real situation in the  $S_{A1}$  phase.

An alternative model for an  $S_{A1}$  phase from polar anisotropic molecules is a variation on the  $S_{\tilde{A}}$  structure. It consists of  $S_{A2}$  regions separated by "walls" as in the  $S_{\tilde{A}}$  phase, in which the double layer structure shifts over a single molecular length, but with a random distribution of walls. The phase transition  $S_{\tilde{A}}S_{A1}$  then corresponds to an order-disorder transition of the walls. Such a model predicts the  $S_{A1}$  phase to be antiferro-electric, though weaker than the  $S_{A2}$  phase. As far as experimental evidence is available, this seems indeed to be the case [12].

Recent high-resolution surface X-ray reflectivity measurements show that for a particular  $S_{A1}$  phase, two or three  $S_{A2}$ -like double layers exist at the surface, in spite of the single-layer X-ray reflection in the bulk [17]. The reconstructed electron density is shown in Fig. 8. The correlation length varies around the  $NS_{A1}$  phase transition from 4 to 6 molecular lengths, in quantitative agreement with the behavior of the diffuse scattering from  $S_{A2}$ -like fluctuations in the bulk. In the above-mentioned model this probably indicates that the walls are expelled from the surface, which thus reveals the underlying short-range structure. If this

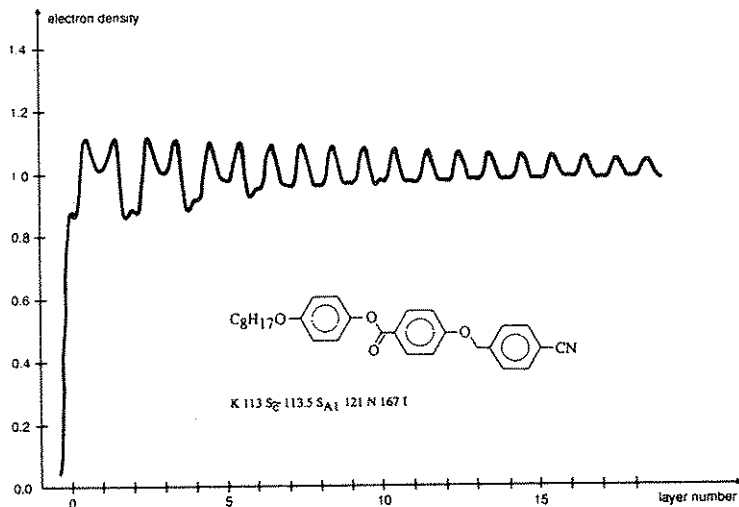


Fig. 8. Reconstructed electron density at 0.8°C above the  $NS_{A1}$  phase transition.

interpretation is correct, two microscopically rather different  $S_A$  phases exist with both  $d \approx \lambda$ , and as far as known the same macroscopic symmetry. One is the "classical"  $S_A$  phase discussed in section 1 with molecules that, if not symmetric by themselves, have locally a random up-down distribution, and secondly an  $S_{A1}$  phase from asymmetric polar molecules that has locally a double layer structure. Interestingly, there are recent indications that the critical behavior of the latter  $NS_{A1}$  phase transition differs from the former  $NS_A$  and the  $NS_{Ad}$  phase transitions [18].

#### 4. CONCLUSIONS

The tendency of aromatic and aliphatic parts of the molecules to segregate is taken as the basic mechanism for the formation of the smectic density modulation. In combination with optimal packing and minimal dipolar repulsions this provides at least a qualitative understanding of the molecular organization of the various types of smectic-A phase, both for effectively symmetric and for asymmetric molecules. In particular, it is shown that probably two rather different ways of molecular ordering can lead to a smectic-A phase with  $d \approx \lambda$ . The implications of this result in terms of miscibility and of critical behavior around the nematic-smectic-A phase transition have not fully been investigated yet.

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