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THE SMECTIC C PHASE OF LIQUID CRYSTALS (*)

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Résumé. — La transition smectique A-smectique C est analysée à partir d'un modèle basé sur l'interaction dipôle-dipôle des liaisons polaires des molécules, qui possèdent un mouvement de rotation autour de leur axe. On utilise deux types différents de fonction de distribution à deux particules, et dans chaque cas on introduit le type de fluctuations approprié. Dans les deux cas, en utilisant une méthode du champ moyen, on trouve que la transition peut être du 1^{er} ordre ou du 2^e ordre. On compare le modèle aux résultats expérimentaux.

Abstract. — The possibility of the smectic A to C phase transition is discussed, using a model based on the dipole-dipole interaction of the polar bonds of the molecules, which are supposed to rotate randomly around their long axis in both the A and C phases. Two different choices of the two-particle distribution function are used, and in each case the appropriate fluctuations involved in the transition are taken into account. In both cases, in the meanfield approximation, we find that the A to C transition can be of first or second order. The model is then compared with experimental results.

1. Introduction. — The explanation of the many liquid crystal phases is an interesting and complicated physics problem, attacked by many authors in recent years. (To introduce the reader to the various liquid crystal phases or mesophases and their properties we refer to de Gennes' book [1].) In this paper we will be concerned with the transition from a smectic A to a smectic C and with terephthal-bis-butyl aniline (TBBA) as an example [2, 3], since this is one of the most studied materials and since it presents a number of different phases.

Theories [4-6] of the nematic and smectic A phases have been proposed in the literature. It has been widely accepted [1] that Van der Waals forces [4] are the interactions responsible for the appearance at least of the nematic phase. An interesting problem in physics is to understand the transition between the uniaxial smectic A and the biaxial smectic C. McMillan [7] suggested that once the smectic A phase is set, an electrostatic dipole-dipole interaction between the polar C-N bonds on neighbouring TBBA molecules

becomes important. At a certain temperature these bonds orient parallel to each other, and this makes the molecules tilt with respect to the smectic layer. In essence, in McMillan's model [7] each molecule is a biaxial object : the biaxiality of the C phase is only a consequence of the fact that the rotational degree of freedom of the molecules around their long axis freezes out at the smectic A to C transition temperature.

At about the same time experimental evidence [8] on NMR spectra of TBBA became available, suggesting that this rotational degree of freedom is not frozen in the smectic C ; later [9] neutron scattering experiments on deuterated TBBA suggested that this is true even for the lower temperature H phase.

In recent papers Priest [10, 11] has shown that a collection of molecules, each described by a second rank axially symmetric tensor, can undergo a phase transition from the uniaxial smectic A phase to the biaxial C phase. He found that the tilt angle saturates at low temperature to a maximum value in agreement with experiment. The interaction between two molecules is assumed [10] to have the same angular dependence as between two axially symmetric quadrupole

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moments. Van der Waals forces may also contribute with a similar dependence on angles [12].

We want to stress that a common difficulty of any model of the A-C transition is the choice of the two-particle distribution function. Usually, to make the problem tractable, this must be introduced *ad hoc* in the model. In a usual crystal the neighbour distance is a temperature dependent property unambiguously determined by this function. In a liquid crystal each molecule is an elongated object; therefore the question arises as to which of the following quantities is more fundamental: the distance between the long axes or the distance between the centres of mass of nearest neighbours. In previous theories [7, 10, 11] this question has been disregarded and the distance between centres of mass has been considered implicitly as fundamental.

The purpose of the present work is to show that the transition from smectic A to smectic C can be understood if we consider the electrostatic interaction between the polar bonds of neighbour molecules in a new way, different from McMillan's. We assume that only the component of the dipole moments parallel to the long molecular axis contributes to such interaction; this should be an approximation to the recent experimental results [8, 9] suggesting the random rotation around this axis; this rotation is assumed to average out the perpendicular component in *both* the A and C phases. Each molecule is, therefore, as in Priest's theory and in accordance with experiment, an axially symmetric object. As for the two-particle distribution function, we analyse two different cases, as explained below.

Our simplifications of reality in the building of the model are perhaps quite naive, but nonetheless we believe the interactions we retain might be just what is needed to give a reasonable picture of the A to C transition. Furthermore, the dipole-dipole interaction has a simple enough form, so that one can very easily visualize its effect in the A and C phases.

2. The model. — We suppose that each molecule has two opposite dipoles. For example, in the case of TBBA, the two C = N double bonds have a dipole moment of 3×10^{-18} esu [13] and the dipoles are directed along a direction making an angle of $\sim 30-40^\circ$ with the long molecular axis. In accordance with experiment, the molecules are supposed to

rotate along their long axis and therefore the perpendicular component of the dipoles is averaged out by the random rotational motion. There remain two oppositely oriented dipolar components along the axis of rotation. We will see below that once the nematic and the smectic A order have been established, there is a tendency of the molecules to tilt (C phase) due to the dipole-dipole interaction.

One could envisage the onset of the tilt of the molecules at the A-C transition, in different ways:

i) the distance D between the molecular axes of neighbour molecules remains constant, but the distance R between the molecular centres increases with the tilt angle α ; this is what we call a *sliding* effect;

ii) the distance R remains constant and D decreases with α ;

iii) these two ways should in general be superposed with each other and with a thermal expansion, in a given material. This thermal expansion could exist also in the A phase and it is not related to the onset of the tilt in the C phase.

Clearly each of these different cases implies a choice of the two-particle distribution function used in the model. Here, from now on, we will restrict ourselves only to i) and ii).

It seems intuitive that such choice is also physically related to the type of fluctuations present near the A-C transition. In case i) each molecule can fluctuate out of the smectic layer, its axis pointing more or less always in the same direction; this means that the nematic order is quite well set and the nematic fluctuations are very small. In case ii) the contrary is true and the molecule fluctuates mostly in a rotational motion around its centre, whereas the smectic order is well set.

We start from the usual dipole-dipole interaction

$$\frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{|\mathbf{r}_1 - \mathbf{r}_2|^3} - 3 \frac{(\mathbf{p}_1 \cdot \mathbf{r}_{12})(\mathbf{p}_2 \cdot \mathbf{r}_{12})}{|\mathbf{r}_1 - \mathbf{r}_2|^5}.$$

Then we write the electrostatic energy of four dipoles on two molecules, shown schematically in figure 1 as small arrows in the body of the molecules (which are represented by elongated cylinders). This energy is readily written as a function of α

$$E_{12} = \frac{p^2}{R^3} \left[2 - 6 \sin^2 \alpha \sin^2 \varphi + \frac{3 \left(1 - \frac{R}{l} \sin \alpha \sin \varphi \right)^2 \frac{R^3}{l^3}}{\left(1 + \frac{R^2}{l^2} - \frac{2R}{l} \sin \alpha \sin \varphi \right)^{5/2}} + \frac{3 \left(1 + \frac{R}{l} \sin \alpha \sin \varphi \right)^2 \frac{R^3}{l^3}}{\left(1 + \frac{R^2}{l^2} + \frac{2R}{l} \sin \alpha \sin \varphi \right)^{5/2}} - \frac{\frac{R^3}{l^3}}{\left(1 + \frac{R^2}{l^2} - \frac{2R}{l} \sin \alpha \sin \varphi \right)^{3/2}} - \frac{\frac{R^3}{l^3}}{\left(1 + \frac{R^2}{l^2} + \frac{2R}{l} \sin \alpha \sin \varphi \right)^{3/2}} \right]. \quad (2.1)$$

FIG. 1. — Two molecules, represented as cylinders, tilted at an angle α in the C phase. The arrows represent the components of the dipolar bonds along the long axis.

If the molecules are tilted in the $Y-Z$ plane, φ is the angle between the X axis and the radius vector of molecule 2 with respect to molecule 1.

In (2.1), p is the magnitude of each dipole, l is the distance between the two dipoles of the molecule. Now, if we consider the case that R is independent of φ and α , the φ and α dependence of E_{12} is explicit in (1); however, in the case that D is independent of φ and α , R depends on these angles according to

$$R = D(1 - \sin^2 \varphi \sin^2 \alpha)^{-1/2}. \quad (2.2)$$

To calculate the total energy per molecule, we shall make the following assumptions :

1) The interaction between layers is neglected : the distance between two nearest dipoles on different planes is $15 \text{ \AA}$, compared with the $5 \text{ \AA}$ distance on the same plane (these data are for TBBA) and the dipole-dipole interaction falls off as the distance cubed. The interaction between layers should therefore be about one order of magnitude smaller than the one between two neighbour molecules.

2) We shall restrict the interaction to the nearest neighbour pairs only.

The total energy per molecule is

$$E_C = \frac{1}{4\pi} \int_0^{2\pi} E_{12} d\varphi. \quad (2.3)$$

The calculation of E_C will be different in the two cases D independent of φ and α or R independent of φ and α . In each case the choice of the two-particle distribution function is implied, as explained above. The calculation of E_C can be performed numerically and we show E_C as a function of α in the two cases : a) $D = \text{constant}$, b) $R = \text{constant}$, in figure 2. (We choose $l = 7 \text{ \AA}$, $D = R = 5 \text{ \AA}$ in the smectic A

FIG. 2. — Energy E_C in units of p^2/l^3 of the molecular dipoles in the C phase : a) when D is constant and equal to $5 \text{ \AA}$; b) when R is constant and equal to $5 \text{ \AA}$. l is always $7 \text{ \AA}$.

phase : these values are approximately right for TBBA.) The two curves exhibit a minimum but in the second case this minimum is much more marked. For small α , E_C decreases as α increases : this is because the interaction between the two upper and the two lower dipoles is dominant at small α and the tendency of dipoles a_1 - a_2 and b_1 - b_2 is to be parallel to the line joining them. In the absence of the a-b interaction the tilt would reach 90° . But because of the electrostatic a-b repulsion, a minimum of E around 60° is reached in both cases. Experimentally, the saturation value of α is always between 35° and 50° . This means that this value is not determined only by the dipole-dipole interaction. We shall discuss this point again below.

3. Free Energy and the A-C phase transition. —

3.1 FIRST CASE : D IS CONSTANT. — We shall begin with the case where the molecules are sliding in the smectic C phase, i.e. the distance between the molecular axes is kept constant. Since the smectic order

FIG. 3. — Allowed fluctuation of one molecule out of the smectic layer.

is not complete, we have to introduce the energy due to the smectic order, and the fluctuations associated to it. To accomplish this we consider the energy of one molecule in a mean field due to all the others, when it fluctuates out of the smectic layer by an amount ε (Fig. 3), maintaining its orientation. The energy is then composed of two terms : the first is the smectic energy E_A , which can be expressed as :

$$E_A = S(\rho) + K\rho \frac{\varepsilon^2}{D^2} \quad (3.1)$$

in (3.1) ρ is the smectic order parameter and, $S(\rho)$ is the mean field energy of one molecule in the layer ; the second term is the contribution of the fluctuations to the energy of the smectic order. This term is even in ε for obvious reasons of symmetry. For stability reasons, K must be positive. E_A in the form (3.1) is the same as a mean field potential used in a microscopic theory of the A phase [5], when the nematic order is well set (order parameter = 1), and for small fluctuations of the molecule near its equilibrium position in the smectic layer. The second contribution to the mean field energy is the dipole-dipole interaction E_C . In the preceding section this term was calculated for $\varepsilon = 0$ using (2.1) and (2.3) and shown in figure 2a. If now ε is supposed to be small (the system is far enough from the nematic-smectic A transition), we can expand E_C in powers of ε . One can show that the linear term in ε is zero and E_C is given by :

$$E_C = F(\alpha) + \frac{\varepsilon^2}{D^2} G(\alpha). \quad (3.2)$$

The functions F and G are even in α . The calculation of $G(\alpha)$ is very cumbersome and will not be given here. For the following we only need to note that $G(0) < 0$,

$$(1/\alpha) (\partial F/\partial \alpha)_{\alpha \rightarrow 0} \rightarrow f < 0$$

and

$$(1/\alpha) (\partial G/\partial \alpha)_{\alpha \rightarrow 0} \rightarrow g > 0.$$

(f and g are constants.)

The free energy per molecule is

$$H = -kT \ln \int_{-\varepsilon_m}^{+\varepsilon_m} e^{-\beta E} d\varepsilon. \quad (3.3)$$

In (3.3), $E = E_A + E_C$ and $\beta = 1/kT$. The limits of integration are $\pm \varepsilon_m$, which could be roughly equal to half the molecular layer width, if the molecule belongs to the layer. H will be expressed as a function of ρ and α , which have to be chosen in a way as to minimize H . Without large error (if K is large enough) we can take infinite limits of integration in (3.3) and we have

$$H = S(\rho) + F(\alpha) - kT \ln \times \int_{-\infty}^{+\infty} d\varepsilon \exp \left\{ -\beta [G(\alpha) + K\rho] \frac{\varepsilon^2}{D^2} \right\}. \quad (3.4)$$

After integration and keeping only the terms which are dependent on ρ and α , we find

$$H = S(\rho) + F(\alpha) + \frac{kT}{2} \ln [G(\alpha) + K\rho]. \quad (3.5)$$

In order to verify whether the A-C phase transition occurs, we expand (3.5) in powers of α around $\alpha = 0$ and the coefficient of α^2 is found to be equal to

$$\frac{1}{2} f + \frac{1}{4} \frac{gkT}{G(0) + K\rho}. \quad (3.6)$$

ρ is the smectic order parameter and therefore it varies slowly with T near the A-C transition. At low T (3.6) is negative because f is negative ; as T increases, (3.6) can change sign since K is supposed to be positive and large. At T_c (3.6) is zero.

The equations giving ρ and α are

$$\frac{\partial H}{\partial \rho} = \frac{\partial S}{\partial \rho} + \frac{kT}{2} \frac{K}{G(\alpha) + K\rho} = 0 \quad (3.7)$$

$$\frac{\partial H}{\partial \alpha} = \frac{\partial F}{\partial \alpha} + \frac{kT}{2} \frac{\partial G/\partial \alpha}{G(\alpha) + K\rho} = 0. \quad (3.8)$$

The last equation can be written as

$$\alpha \left[\frac{1}{\alpha} \frac{\partial F}{\partial \alpha} + \frac{kT}{2} \frac{\frac{1}{\alpha} \frac{\partial G}{\partial \alpha}}{G(\alpha) + K\rho} \right] = 0. \quad (3.9)$$

This shows the possibility of having two types of solution for (3.9). One is $\alpha \equiv 0$ corresponding to the smectic A. The other solution corresponding to the C phase is obtained by dividing (3.9) by α and solving together with (3.7). The transition temperature T_c and the value of ρ at T_c are given by

$$f + \frac{kT_c}{2} \frac{g}{G(0) + K\rho_c} = 0 \quad (3.10)$$

and

$$\left(\frac{\partial S}{\partial \rho} \right)_{\rho_c} + \frac{kT_c}{2} \frac{K}{G(0) + K\rho_c} = 0. \quad (3.11)$$

From (3.11) and (3.7), we see that $(\partial S/\partial \rho)$ is negative, i.e. the energy of the smectic order decreases if ρ increases, as is expected.

In order to determine whether the transition is of first order or of second order, we shall calculate α^2 , in the vicinity of T_c . If $d(\alpha^2)/dT$ is negative, the transition is of second order, if it is positive the transition is of first order. We expand $\partial S/\partial \rho$ around ρ_c , and the functions $(1/\alpha) (\partial F/\partial \alpha)$ and $(1/\alpha) (\partial G/\partial \alpha)$ around $\alpha = 0$. From (3.7-9) we get :

$$\begin{aligned} & \left(\frac{\partial S}{\partial \rho} \right)_{\rho_c} + s(\rho - \rho_c) \\ & + \frac{kT}{2} \frac{K}{G(0) + \frac{1}{2} g\alpha^2 + K\rho_c + K(\rho - \rho_c)} = 0 \end{aligned} \quad (3.12)$$

(where

$$S(\rho) \simeq S(\rho_c) + (\partial S/\partial \rho)_{\rho_c} (\rho - \rho_c) + \frac{1}{2} s(\rho - \rho_c)^2 + \dots$$

and

$$f + f' \alpha^2 + \frac{kT}{2} \frac{g + g' \alpha^2}{G(0) + \frac{1}{2} g \alpha^2 + K \rho_c + K(\rho - \rho_c)} = 0 \quad (3.13)$$

where $\frac{1}{4} f' \alpha^4$ and $\frac{1}{4} g' \alpha^4$ are the fourth-order terms in α of $F(\alpha)$ and $G(\alpha)$. We solve (3.12, 13) keeping only the linear term in $(\rho - \rho_c)$ and quadratic in α . After a straightforward calculation, we get

$$\alpha^2 = - \frac{k}{2} \frac{(T - T_c) [gB - fK^2]}{AB - \frac{1}{2} fg(\partial S/\partial \rho)_{\rho_c} K} \quad (3.14)$$

where $A = fg/2 + f'[G(0) + K\rho_c] + kT_c g/2$ and $B = s[G(0) + K\rho_c] + K(\partial S/\partial \rho)_{\rho_c}$.

Depending on the values of the different parameters, $d(\alpha^2)/dT$ can be positive or negative, i.e. we can get either a first or a second order transition. Now when $T \rightarrow 0$, ρ tends to its low temperature value and from (3.9), α goes to the value which minimizes the function F , i.e. $\alpha_m \simeq 58^\circ$, as seen in figure 2a. As a final remark, in the case that the transition is of first order, T_c is the stability limit of the A phase.

3.2 SECOND CASE : R IS CONSTANT. — Now the smectic order is supposed to be perfect but the fluctuations of the molecules are those of the angle θ of the molecular axis with respect to the mean direction of all the other molecules. This mean direction defines the tilt angle α . The procedure of the calculation is as above. The energy is decomposed into two parts and we express explicitly the contribution due to the fluctuations. We have $E_N = n(\eta) + v\eta\theta^2$ and $E_C = F_1(\alpha) + \theta^2 G_1(\alpha)$, where η is the nematic order parameter and the linear term in θ can be shown to be zero.

The conclusions are clearly identical to the preceding discussion and we get a phase transition which can be of first order, or second order. At $T = 0$ α goes to $\alpha_m = 62^\circ$, as indicated in figure 2 by curve b. To end this section, we note that ρ and η exhibit a discontinuity if the transition is of first order or a discontinuity in the temperature derivative, if the transition is of second order.

4. Comparison with the experimental results. — Clearly we can compare our results only with materials whose molecules can be correctly described by a set of two opposite dipoles. We assume that, due to its molecular structure, this is the case for TBBA. Numerous experiments have been performed on this material and it is instructive to try a comparison with

our results. We shall discuss essentially two points : the mechanism of the A-C phase transition and the saturation value α_m of the tilt angle.

We have distinguished between the two extreme cases : D constant and R constant. In fact in TBBA it seems that the two mechanisms occur together. This conclusion is drawn from the recent results of Guillon and Skoulios [14].

They have measured the molecular area S inside the smectic layer in the A and C phases. When T is lowered S decreases slowly in the A phase, then it increases in the C phase, at first sharply and soon it saturates. In the A phase the molecular area σ perpendicular to the molecular axis is equal to S . From the relation

$$\sigma = S \cos \alpha$$

valid in the C phase, and assuming an extrapolation of σ from the A to the C phase, they are able to deduce the variation of the tilt angle with the temperature. The results are in good agreement with other measurements obtained with different methods.

What does this experiment imply as far as our model is concerned ? First in the A phase a slow decrease (as T is lowered) of $\sigma (= S)$, means a correspondingly slow decrease of $D (= R)$. Then, in the C phase, D keeps decreasing slowly (since σ decreases slowly) and R increases sharply with the sharp increase of S : therefore, we have a strong sliding effect of the molecules and our model with $D = \text{constant}$ for the onset of the C phase should apply, until S starts to saturate $\sim 20^\circ$ below T_c . The slow decrease in D is not essential to understand the onset of the C phase because it is probably due to the thermal expansion, and therefore it is not taken into account in the model. When S starts to saturate, R saturates too, probably because of attractive interactions like Van der Waals forces which oppose large values of R . Now the model at constant R should apply, but the short range steric repulsion can come into play by limiting the value of D to the molecular diameter d . In fact, since now R is constant, figure 2b shows that α should reach a value $\alpha_m \sim 60^\circ$. However, the steric effect imposes the relation $\cos \alpha_m = d/R$.

We shall take the following values for TBBA : $d \simeq 4.3 \text{ \AA}$ and $R \simeq 5.2 \text{ \AA}$ in the tilt plane in the C phase (R is taken from the data of Doucet *et al.* [15]), d is evaluated simply from the bond lengths of the benzene rings [13]. We get $\alpha_m = 34^\circ$, which is very close to the experimental value and far from the 60° predicted by the dipole-dipole interaction. Such good agreement with the saturation value of α at low T (ref. [3]) indeed suggests that the steric effects are important, even though they are usually neglected in the calculations, especially at large tilt angles.

An indication as to which of the two possible modes ($D = \text{constant}$ or $R = \text{constant}$) is more important, can be obtained also by measuring the critical fluctuations in the smectic A phase, as explained by Delaye

and Keller [16]. Measuring the quasielastic Rayleigh scattering can give information on the nature of the fluctuations : layer undulations or molecular tilt. Delaye and Keller have actually observed molecular tilt fluctuations at the A-C phase transition of undecylclazoxymethylcinnamate. This suggests that the transition may take place according to the picture with $R = \text{constant}$, in this case.

5. Conclusion. — We have presented a model of the A-C phase transition based on the dipole-dipole interaction and in which the molecules are rotating around their long axis. To explain the onset of the smectic C phase we have considered two different possible mechanisms : in the first there is a sliding of the molecules on one another (the distance between axes remaining constant), in the second the molecules tilt but keep the distance between their centres constant. Which mechanism is working at the transition depends on what kind of fluctuations are present in the smectic A phase : layer undulations or molecular tilt.

They could of course, in general, occur together. We have suggested that the electrostatic interactions due to the polar bonds of the molecules can play a major role in establishing the smectic C phase in a way different from McMillan's view [7] and more similar to Priest's [10, 11]. However, in order to explain the experimentally observed value of α_m at low T , we see that other types of forces are to be taken into account : Van der Waals attractive forces and short range repulsive forces. The experiments on TBBA show how complicated reality is with respect to any simple model that can be worked out. On the other hand one can at least explain the onset of the C phase with well known interactions and reasonable assumptions ; in such a way we hope that we can distinguish between the important features of the phenomenon and the ones which are marginal.

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