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AN INDUCED DIPOLE MODEL OF THE SMECTIC C PHASE

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Résumé. — Un modèle de la phase smectique C est proposé dans lequel l'inclinaison est supposée avoir son origine dans les forces entre dipôles et dipôles induits. On a supposé que la rotation autour du grand axe moléculaire est libre. Trois phases alignées ont été trouvées correspondant à la phase smectique C, la phase smectique A et la phase nématique. L'entropie d'entassement joue un rôle important dans le mécanisme de la transition smectique A-smectique C. Cette transition n'est pas du type connu ordre-désordre.

Abstract. — A model of the smectic C phase is proposed in which the tilt is thought to originate from the forces between dipoles and induced dipoles. The rotation about the long axis is assumed to be free. Three ordered phases are found corresponding with the smectic C phase, the smectic A phase and the nematic phase. The entropy of packing plays an important role in the mechanism of the smectic C-smectic A phase transition. This transition is not of the usual order-disorder type.

1. Introduction. — In the smectic A and C phases the distribution of the centres of mass within the layers is random. The smectic A phase is optically uniaxial. The smectic C phase is found to be biaxial. According to the Landau theory of de Gennes [1] the director coincides with the plane normal in the A phase, whereas there is a tilt angle between the layer normal and the director in the C phase. In the present paper we will adhere to this point of view. The existing models of the smectic C phase are those of McMillan [2], Wulf [3], Priest [4] and of Cabib and Benguigui [5]. A short review of these models is given in the table I. Vertically distinction is made between models in which the rotation about the long molecular axes is assumed to be frozen out in the C phase and models which allow free rotation. Horizontally we mentioned the different forces which are believed to cause the biaxial nature of the C phase.

Goodby, Gray and McDonnell [6] and de Jeu [7] studied the influence of dipoles and steric factors upon the stability of the smectic C phase. The results of their structural studies do not support the models of Wulf and of Cabib and Benguigui, but reveal the importance of transverse dipoles. Their observations can be interpreted in terms of McMillan’s dipole model or in terms of an extension of that model due to de Jeu [7]. Experiments that probe the rotational motion of the molecules about their long axes show that the rotational bias is very small in the smectic C phase [8]. This is consistent with an almost negligible biaxiality with respect to the director as is seen in the polarizability [9]. These data put the models of McMillan and Wulf in serious doubt. The theory of Priest is based on a general coupling between 2nd rank tensors and is consistent with the experimental results mentioned above. He showed how one can describe the smectic C phase microscopically without the need for a freeze-out of the rotations about the long axes. However, he does not discuss the relation between his coupling constants and the molecular structure.
Moreover the mechanism for the transition from the smectic C phase to the smectic A phase in his model is not very clear.

In all the models of the smectic C phase the translational order is essentially considered to be constant and the main interest is to describe the CA transition. Materials with large tilt angles do not exhibit a transition to the A phase, but directly change to the nematic (N) or isotropic (I) phase with increasing temperature [10]. In order to explain this effect it is obviously of interest to study a model that contains all four phases.

The purpose of the present paper is to propose a new physical picture of the smectic C phase: the induction forces between (transverse) dipoles and the polarizable centres of neighbouring molecules induce a tilt in the system. As a result the nearest neighbour distance in the plane increases due to excluded volume effects. This increase is energetically unfavourable as far as the attractions between polarizable centres are concerned. If the induction forces are strong enough, a smectic C phase will be formed. Free rotation does not destroy the smectic C phase, because the induction forces do not average out in that case. To rationalize this picture we introduce in the next section an interaction model in which the molecular shape and the dipoles and induced dipoles play an important role. A Molecular Field Approximation (MFA) is given in section 3. The solutions of the equations of the MFA are presented in section 4 using the approximation that the orientational order is constant in the smectic phases. The model exhibits three ordered phases, the C, A and N phases, and one disordered phase, the I phase. The CA transition is not of the usual order-disorder type. The mechanism is that the entropy of packing together with the average attractions between the polarizable centres overcome the internal energy associated with the induction forces at the transition temperature. If the latter forces are very strong, the tilt angle will be large and its temperature-dependence will be small, and the A phase is not stable at any temperature. The last section contains a discussion of the results and a comparison with relevant experiments.

2. The model. — Consider an elongated molecule as found in liquid crystals. Let us first ignore the dipoles. The molecules often have alkyl- or alkoxy-tails and a central part where the polarizability is largely concentrated. McMillan [11] used this picture to explain why the central parts tend to collect in a plane. Calculations of Gelbart and Gelbart [12] support such a picture. They showed that the orientational dependence of the potential is largely due to the coupling between isotropic attractive interactions and anisotropic hard core repulsions. As mentioned already there is experimental evidence that the molecules rotate rapidly about their long axes. This leads us to the following simplified picture of the molecule: it is a rodlike object without a distinguishable head or tail, having an isotropic polarizability in its centre. Effectively the intermolecular forces are not likely to have a long-range character. Consequently the interactions between neighbouring molecules and j can be considered to be only dependent upon the nearest neighbour distance or closest distance of approach, $\xi(i,j)$. This distance varies between the molecular breadth $B$ and length $L$. It is a complicated function of the orientations of the long molecular axes of i and j, denoted by the unit vectors $a_i$ and $a_j$, respectively, and of the direction of the intermolecular distance vector, given by a unit vector $u_{ij}$ pointing from the centre of i to that of j. For a nearest neighbour interaction which only depends upon $\xi(i,j)$, we can immediately derive the following properties:

1) If $a_i \perp u_{ij}$ and $a_j \perp u_{ij}$,
$$V(\xi(i,j)) = V(B),$$
irrespective of the value of $a_i \cdot a_j$!

2) If $a_i \not\perp u_{ij}$ and $a_j \perp u_{ij}$,
$$V(\xi(i,j)) = V(\frac{1}{2} L + \frac{1}{2} B).$$

3) If $a_i \not\perp a_j$ and $(a_i \cdot u_{ij})^2 = (a_j \cdot u_{ij})^2 = \sin^2 \omega$ and $\omega$ small,
$$V(\xi(i,j)) = V(B \cos \omega) = V(B) + \frac{1}{2} B \frac{dV}{d\xi} \sin^2 \omega + \frac{1}{3} B \frac{d^2V}{d\xi^2} + \frac{1}{2} B^2 \frac{d^2V}{d\xi^2} \sin^4 \omega$$
where both derivatives are taken at $\xi = B$.

It is reasonable to expect $V(L) \approx V(\frac{1}{2} L + \frac{1}{2} B)$. This suggests the following order of magnitude estimate:
$$V(\frac{1}{2} B + \frac{1}{2} L) - V(B) \approx \frac{1}{2} B \frac{dV}{d\xi} (at \xi = B) \sim \frac{3}{2} B \frac{dV}{d\xi} + \frac{1}{2} B^2 \frac{d^2V}{d\xi^2} (at \xi = B) \sim$$
the energy to remove a molecule from the smectic plane $\approx k_B T$, where $k_B$ is Boltzmann's constant and $T$ is a temperature typical for the liquid crystalline phases i.e. $T \sim 300$ (400) K. The quantity $-V(B)$ is approximately equal to the heat of vaporization $\approx k_B T$. On the other hand we can expand $V(\xi(i,j))$ in spherical harmonics. It is a helpful approximation to retain only the first relevant terms, i.e. we assume that $V(\xi(i,j))$ can be written as a coupling between 2nd rank tensors. Confining ourselves to achiral molecules, we can write the nearest neighbour interaction as a linear combination of six rotational invariants [13]. A comparison with the three properties derived above allows us to determine the coefficients.

The result is:
$$V(\xi(i,j)) = -v_0 + v_1(a_i \cdot u_{ij})^2 + v_2(a_j \cdot u_{ij})^2$$
$$- (2v_1 - v_2)(a_i \cdot a_j)(a_j \cdot u_{ij})(a_j \cdot u_{ij})$$
$$+ v_3(a_i \cdot u_{ij})^2(a_j \cdot u_{ij})^2$$
(2.1)
with
\[ v_0 = -V(B), \quad v_1 = V(\frac{1}{2} B + \frac{1}{2} L) - V(B), \]
\[ v_2 = \frac{1}{6} B \frac{dV}{d\xi} \text{ at } \xi = B \]
and
\[ v_3 = \frac{8}{6} B dV/d\xi + \frac{8}{6} B^2 d^2V/d\xi^2 \text{ at } \xi = B. \]

Next we place a dipole on the axis of one of the molecules. The dipole induces a dipole in the centre of the neighbouring molecule. The dipoles attract each other. In order to estimate the effect of this induction interaction we take the central polarizability as a point polarizability \( \alpha \) of the order of 100 \( \text{Å}^3 \). We estimate the dipole moment to be about 2.5 Debye and we take the minimum nearest neighbour distance \( B \) equal to 5 \( \text{Å} \). The induction energy is proportional to
\[ \alpha\mu^2 B^{-6} \approx 0.03 \text{ eV} \sim k_B T. \]

The molecules rotate rapidly about their long axes

\[ V_{\text{au}} = -\frac{1}{2} \alpha\mu^2 B^{-6}(1 + x^2)^{-6} [(x^2 + 1)^3 + (2x^6 + 10x^4 - 12x^2) - 1 + (7x^4 - 2x^2 + 1) P_2(a_i.p_i)] (a_i.u_i)^2 \]  
(2.3)

where \( x = d/B \) and \( d \) is the distance between the dipole and the centre of the same molecule. Note that the coefficient of \( (a_i,u_i)^2 \) in eq. (2.3) has the following properties: for \( P_2(a_i,p_i) = 1 \) (longitudinal dipole) its optimal value is \( -0.1 \alpha\mu^2 B^{-6} \) at \( x = 1.0 \), for \( P_2(a_i,p_i) = 0 \) (the angle between the dipole and the long axis is 54.7°) its optimal value is \( -0.3 \alpha\mu^2 B^{-6} \) at \( x = 0.7 \) and for \( P_2(a_i,p_i) = -\frac{1}{2} \) (transverse dipole) its optimal value is \( -0.5 \alpha\mu^2 B^{-6} \) corresponding with \( x = 0.6 \). Formula (2.3) indicates that an acentral dipole and in particular an acentral transverse dipole induces the tendency for the long axis to tilt towards the direction of the line connecting the centre of the molecule and that of its neighbour. This tendency is described by a term \( -w(a_i,u_i)^2 \) in the situation of figure 1. In the general case it is slightly more complicated. However, without loss of the essential physics we can retain this simple type of interaction. It is understood here that \( w \) is a function of \( d, B, L \) and \( (a_i,p_i)^2 \) and that \( w \) obtains an optimal value if the dipole is placed somewhere in the middle between the centre and one of the ends of the molecule. If more dipoles are present, they all contribute to \( w \). If both molecules have dipoles we must add a term
\[ -w(a_i,u_i)^2 - w(a_j,u_j)^2 \]
to eq. (2.1). We can now complete our model of the nearest neighbour interaction. It is a superposition of \( V(\xi(i,j)) \), the combination of isotropic attractions and hard core repulsions, and the terms associated with the dipoles. The induction energy contributes to \( v_0 \) as well, but this term is not relevant.

The interaction model can explain the tendency for a smectic phase. To illustrate the point consider two molecules with their long axes parallel to each other as in figure 1. The tilt angle is \( \omega \). According to our model the energy associated with this state is
\[ V(\omega) = -v_0 + (v_2 - 2w) \sin^2 \omega + v_3 \sin^4 \omega. \]  
(2.4)

If \( w/v_2 < \frac{1}{2} \), \( V(\omega) \) is minimal for \( \omega = 0 \). This situation corresponds with an organization as in the smectic \( \text{A} \) phase. Note that in the Kobayashi-McMillan model [11], which does not contain terms that couple the orientations of the long axes with the direction of the distance vector, the energy of the state pictured in figure 1 is independent of \( \omega \). That means, that their model does not contain a force which keeps the long axes perpendicular to the layers. Similar arguments against the Kobayashi-McMillan model have been given recently by Priest [14]. If \( w/v_2 > \frac{1}{2} \), the energy is minimal for \( \omega \neq 0 \) as in the smectic C phase. According to the estimates above \( v_2 \) is of the order of \( k_B T \).
and \( w \) can also be of the order of \( k_B T \). If, therefore, the dipoles are strong enough and well situated \( w \) can compete with \( v_2 \) and a smectic C phase can be found. In the next two sections the properties of the model introduced here are discussed more quantitatively. This is done on the basis of a MFA.

3. Molecular field approximation. — In the MFA we have to calculate an appropriate average of

\[
V(0) = \sum_{i=1}^{N} V(a_i, \mathbf{u}_i, \mathbf{w}_i),
\]

the potential felt by a central molecule due to interaction with its \( \gamma \) nearest neighbours. The various steps in the calculation are briefly discussed below.

1) The averaging over the directions of the distance vector, \( \mathbf{u}_{0i} \), can be immediately performed in two extremal situations:

a) If the molecular centres are randomly distributed, all \( \mathbf{u}_{0i} \) are equally probable. The average of \( V(0) \) over \( \mathbf{u}_{0i} \) is \( \overline{V(0)}_{\text{iso}} \).

b) If the centres of mass are located in equidistant planes and translate freely in the planes, a fraction \( \alpha \) of the \( \gamma \) nearest neighbours is located in the same plane as the central molecule and for this fraction the endpoint of \( \mathbf{u}_{0i} \) lies on a circle perpendicular to \( \mathbf{e} \), the plane normal, whereas the remaining part of the \( \gamma \) nearest neighbours is situated in the adjacent planes and has essentially \( \mathbf{u}_{0i} \) (anti) parallel to \( \mathbf{e} \). The average of \( V(0) \) over \( \mathbf{u}_{0i} \) in this case is denoted by \( \overline{V(0)}_{\text{planar}} \). The real mean field potential lies somewhere between \( \overline{V(0)}_{\text{iso}} \) and \( \overline{V(0)}_{\text{planar}} \). A central assumption here is that no qualitative error is made if we obtain the average of \( V(0) \) over \( \mathbf{u}_{0i} \) by the following interpolation.

\[
V(0) = \overline{V(0)}_{\text{iso}} + \left[ \overline{V(0)}_{\text{planar}} - \overline{V(0)}_{\text{iso}} \right] \cos \varphi_{0i},
\]

with

\[
\varphi_{0i} = \varphi_0 - \varphi_1 = (2 \pi / t) (r_0 . \mathbf{e} - r_i . \mathbf{e}),
\]

where \( t \) is the layer thickness and \( r_i \) is the position of the centre of molecule \( i \). This interpolation procedure is closely related to the method of expanding the potential in a Fourier series and only keeping, as usually done, the first Fourier components [11]. The parameter \( \alpha \) is comparable with McMillian's

\[
\alpha_d = 2 \exp \left( -\frac{\pi r_0}{t} \right)^2
\]

(\( r_0 \) being the diameter of the polarizable centre) and measures the tendency to form a smectic phase. The nearest neighbours are the molecules within a certain range around the central molecule. This range will be of the order of the molecular length and will be proportional to \( r_0 \). Therefore, the fraction of the nearest neighbours in the plane, \( \alpha \), can be expected to be a decreasing function of \( r_0 / t \) and rather close to unity.

2) We average over the azimuthal angle of \( \mathbf{a}_0 \) and \( \mathbf{a}_i \) with respect to the director \( \mathbf{n} \) (the director is taken constant in space). The resulting expression depends upon the tilt angle \( \alpha \), the angle between the plane normal \( \mathbf{e} \) and the director \( \mathbf{n} \). The averaging over the azimuthal angles is allowed in the smectic A, the nematic and the isotropic phase, but it is not exactly correct in the smectic C phase, which is biaxial. The phase biaxialities with respect to the director in this phase, however, are quite small [9] and it is a good approximation to neglect them entirely.

3) The factors in \( V(0) \) depending on the coordinates of the neighbours are replaced by order parameters. Three order parameters appear: \( \overline{P}_2 \), the average of \( P_2(\mathbf{a}_i, \mathbf{n}), \cos \), the average of \( \cos (2 \pi r . \mathbf{e} / t) \) and \( \overline{P}_2 \) cos, the average of \( P_2(\mathbf{a}_i, \mathbf{n}) \cos (2 \pi r . \mathbf{e} / t) \) (we chose the origin to lie in a smectic plane). The orientational free energy follows immediately and is a function of the temperature, the order parameters and the nematic coupling constant

\[
B_0 = \frac{2}{3} \gamma (2 v_1 - v_2 - \frac{2}{3} v_3)
\]

and the four smectic coupling constants

\[
A_2 = \frac{2}{3} \gamma (v_1 + v_2 + v_3) \left( \frac{3}{2} \alpha - 1 \right),
\]

\[
C_2 = \frac{2}{3} \gamma w \left( \frac{3}{2} \alpha - 1 \right),
\]

\[
B_2 = \frac{2}{3} \gamma (2 v_1 - v_2 - \frac{2}{3} v_3) \left( \frac{3}{2} \alpha - 1 \right),
\]

\[
B_4 = \frac{8}{3} \gamma v_3 \left( -\frac{1}{6} \alpha + 1 \right). \]

4) So far we have neglected the entropy of packing. The problem of how to take this entropy into account in the nematic phase has recently obtained considerable attention [15, 16]. There it behaves as if it were an internal energy proportional to \( \rho \) (the density), to \( k_B T \) and to a suitable (density-dependent) average of the excluded volume. It turns out that inclusion of the packing entropy in the nematic phase results in a renormalization of the anisotropic coupling constant \( B_0 \) [15, 16]: \( B_0 \rightarrow B_0(1 + T / T_p) \), where \( T_p \) may be called the packing temperature. \( T_p \) measures the contribution of steric hindrance to the orientational order. Comparison between theory and experiment indicates that \( T_p \) is of the order of 500 K. In the theory of Maier and Saupe [17] \( T_p \) is infinite. In our model the constants \( A_2, B_0, B_2 \) and \( B_4 \) originate from isotropic attractions modulated by the anisotropy in the shape and correspond, roughly speaking, to certain averages of the excluded volume. This leads us to the assumption that packing influences the coupling constants \( A_2, B_0, B_2 \) and \( B_4 \) in the same way: \( J \rightarrow J(1 + T / T_p) \) with \( J = A_2, B_0, B_2 \) and \( B_4 \). The constant \( C_2 \) corresponds to the effect of the dipoles and is not related to the anisotropy in molecular shape. Packing leaves \( C_2 \) unaltered. With these changes the orientational free energy per molecule becomes
\[ F = \frac{1}{2}(1 + T/T_p) B_0 \bar{P}_2 \bar{P}_2 + \left[ (1 + T/T_p) A_2 - C_2 \right] P_2(\cos \omega) \bar{P}_2 \cos \cos \left[ (1 + T/T_p) B_2 P_2(\cos \omega) \bar{P}_2 \cos \cos \right] - \frac{1}{2}(1 + T/T_p) B_2 P_2(\cos \omega) \bar{P}_2 \cos \cos - \frac{1}{2}(1 + T/T_p) B_4 P_4(\cos \omega) \bar{P}_2 \cos \cos - k_B T \ln Z. \]

\[ Z = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\varphi \int_0^1 d\mathbf{a} \cdot \mathbf{n} \exp(-\beta E), \quad \beta = (k_B T)^{-1} \]

\[ E = -\left( 1 + T/T_p \right) B_0 \bar{P}_2 P_2(\mathbf{a} \cdot \mathbf{n}) - \left[ (1 + T/T_p) A_2 - C_2 \right] P_2(\cos \omega) \left[ \bar{P}_2 \cos \cos \phi + \cos P_2(\mathbf{a} \cdot \mathbf{n}) \cos \phi \right] + \left[ (1 + T/T_p) B_2 P_2(\cos \omega) \bar{P}_2 \cos P_2(\mathbf{a} \cdot \mathbf{n}) \cos \phi + (1 + T/T_p) B_4 P_4(\cos \omega) \bar{P}_2 \cos P_2(\mathbf{a} \cdot \mathbf{n}) \cos \phi \right] \]

where \( P_4 \) is the 4th Legendre polynomial. The effect of the entropy of packing may be interpreted as follows: in the smectic C phase there is more excluded area in the layer than in the smectic A phase and thus less free area for the molecules to jostle around. This means that the entropy of packing disfavours a tilted structure.

The order parameters and the tilt angle are determined by the requirement that the free energy should be minimal with respect to variations in \( \bar{P}_2, \cos, P_2 \cos \) and \( \omega \). The resulting equations form a set of four coupled nonlinear equations. The isotropic solution \( \bar{P}_2 = \cos = P_2 \cos = \omega = 0 \) is always satisfied. In the case that more than one set of solutions exists, the requirement that the free energy should be minimal selects the correct one. The solutions of these equations are discussed in the next section where we use the approximation that the orientational order is constant in the smectic phases.

4. Solutions in the case of constant orientational order in the smectic phases. — In the smectic phases the orientational order is rather high \( (\bar{P}_2 \sim 0.8) \) and varies very slowly with temperature [18]. This suggests that the equations for the order parameters and the tilt angle can be approximately solved taking \( \bar{P}_2 \) constant in the smectic phases. This approximation decouples the translational and orientational order \( (\bar{P}_2 \cos = \bar{P}_2 \cos \cos) \) and the tilt angle. It is correct if the \( T_{NI} \) is considerably higher than the temperatures where the smectic phases are stable. We will apply this approximation here. The expression for the orientational free energy per molecule reduces to a simpler one,

\[ F = F_{\text{nematic}} + F_{\text{smectic}} \]

\[ F_{\text{nematic}} = \frac{1}{2} B_0 (1 + T/T_p) \bar{P}_2 \bar{P}_2 - \frac{1}{2} B_0 \ln \int_0^1 \mathbf{a} \cdot \mathbf{n} \exp \left[ B_0 \beta (1 + T/T_p) \bar{P}_2 P_2(\mathbf{a} \cdot \mathbf{n}) \right] \]

\[ (4.1a) \]

where \( D_0 \) is the 4th Legendre polynomial. The effect of the entropy of packing may be interpreted as follows: in the smectic C phase there is more excluded area in the layer than in the smectic A phase and thus less free area for the molecules to jostle around. This means that the entropy of packing disfavours a tilted structure.

The order parameters and the tilt angle are determined by the requirement that the free energy should be minimal with respect to variations in \( \bar{P}_2, \cos, P_2 \cos \) and \( \omega \). The resulting equations form a set of four coupled nonlinear equations. The isotropic solution \( \bar{P}_2 = \cos = P_2 \cos = \omega = 0 \) is always satisfied. In the case that more than one set of solutions exists, the requirement that the free energy should be minimal selects the correct one. The solutions of these equations are discussed in the next section where we use the approximation that the orientational order is constant in the smectic phases.

The solutions refer to the following phases.

C (the smectic C phase) corresponding with \( \bar{P}_2 \neq 0, \cos \neq 0 \) and \( \omega \neq 0 \).

A (the smectic A phase) corresponding with \( \bar{P}_2 \neq 0, \cos \neq 0 \) and \( \omega = 0 \).

N (the nematic phase) corresponding with \( \bar{P}_2 \neq 0 \) and \( \cos = 0 \).

I (the isotropic phase) corresponding with \( \bar{P}_2 = \cos = 0 \).

In order to present the solutions we introduce

\[ \zeta = C_2(A_2 - \frac{1}{2} B_2 \bar{P}_2)^{-1}, \]

\[ \zeta_c = G\eta(G - 1.4 \bar{P}_2 + 1.4 \eta \bar{P}_2)^{-1}, \]

\[ \eta = 1 - \frac{3}{8} B_4 \bar{P}_2 (A_2 - \frac{1}{2} B_2 \bar{P}_2)^{-1}, \]

\[ G = 2 k_B T \eta (A_2 - \frac{1}{2} B_2 \bar{P}_2)^{-1}, \]

\[ b = 4.542 k_B T \eta \bar{P}_2^{-1} - 1. \]

The parameter \( \zeta \) measures the relative strength of the induction forces and is zero in the absence of dipoles and is of order unity if the induction energy becomes of the order of \( k_B T \). The parameter \( \eta \) represents the resistance against a tilted structure; it varies between unity and zero. We find three cases:

1) \( \zeta < \eta \) A, N, I.
2) \( \eta \leq \zeta \leq \zeta_c \) C, A, N, I.
3) \( \zeta_c < \zeta \) C, N, I.

The corresponding transition temperatures are given below:

\[ T_{CA} = T_{NI} b(\zeta - \eta) \]

\[ T_{AN} = T_{NI} b(1.4 + 0.6 \eta - 2 \zeta) \times \]

\[ (G/\bar{P}_2 - 1.4 - 0.6 \eta)^{-1} \]
\[ T_{\text{CN}} = T_{\text{NI}} b(2(1 - \zeta) P_z(\cos \omega) - 0.6(1 - \eta) \times \]
\[ \times P_x(\cos \omega)) (\overline{b}/2 - 2 P_z(\cos \omega) \]
\[ + 0.6(1 - \eta) P_x(\cos \omega))^{-1} \] (4.4c)
\[ T_{\text{NI}} = T_p b^{-1}. \] (4.4d)

If the tilt angle is nonzero, we have
\[ \sin \omega = \frac{4 (1 + T/T_p)^{-1}} {\sqrt{1 - \eta}} \] (4.5)

The NI and CI phase transitions are not considered here. The NI phase transition is 1st order. The CA phase change is 2nd order. The CN phase transition is found to be similar to the AN phase transition and they are both 2nd order. This is partly due to an artifact of the constant-\(\overline{P}_2\)-approximation. If the isotropic phase is close to the smectic phase one should find a 1st order smectic-nematic phase transition. The 1st order character is due to coupling between translational and orientational order [1, 11]. Another mechanism for a 1st order smectic-nematic transition is the coupling between the first and higher translational order parameters [19]. Typical examples of phase diagrams and tilt angles are presented in the figures 2 and 3.

**Fig. 2.** — (a) Example of a phase diagram with \(\zeta \sim \zeta\) showing the transition temperatures versus the relative strength of the induction energy. The following values are used: \(P_z = 0.800\) in the smectic phases, \(a = 0.860, v_1/v_2 = 1.880\) and \(v_2/v_3 = 1.458\); (b) The tilt angle as a function of temperature near the CA phase transition referring to the diagram in (a) at \(\zeta/\eta = 1.588\).

**Fig. 3.** — (a) Example of a phase diagram with \(\zeta > \zeta\) showing the transition temperatures versus the relative strength of the induction energy. The following values are used: \(\overline{P}_2 = 0.800\) in the smectic phases, \(a = 0.860, v_1/v_2 = 1.465\) and \(v_2/v_3 = 1.634\); (b) The tilt angle as a function of temperature near the CN phase transition referring to the diagram in (a) at \(\zeta/\eta = 8.900\).

5. **Discussion.** — Dipoles and in particular transverse dipoles are important for the stability of the smectic C phase. However, forces between permanent dipoles average out due to (nearly) free rotation about the long axes. In the present model we propose that the forces between dipoles and dipoles induced in the centres of neighbouring molecules produce a tilt in the system. The strength of the anisotropic part of the induction forces is measured by a parameter \(\zeta\). The resistance against tilt is described with a parameter \(\eta\) and originates from a combination of Van der Waals forces and hard core repulsions. If \(\zeta < \eta\) a smectic C phase is possible. Calculations of the forces between a dipole and a neighbouring point polarizability show that \(\zeta\) depends strongly on the position of the dipole at the molecule. In reality the polarizability is smeared out and deviations occur if the dipole is too close to the centre. An acetal dipole and in particular an acetal transverse dipole contributes to \(\zeta\) and there is an optimal location at the molecule. If one changes the chain length of the molecules, one expects that the dipole effectively moves towards or away from his optimal position and that \(\zeta\) changes similarly. This is in qualitative agreement with the results of Goodby and Gray [20]. It would be of interest to investigate the correlation with the thermal stability of the C phase by changing the positions of the dipole directly.

We find agreement with the experimental trend: small tilt, strong temperature-dependence, a CA transition — large tilt, weak temperature-dependence, no CA phase transition [10]. The tilt angles in our model are somewhat too low, however. For instance in the example displayed in figure 2b, \(\omega\) at \(T_{\text{CA}} = 1\) K is about 2° which is smaller than the corresponding value in TBBA of about 5° [21]. Improvement is obtained if one takes the variation of the orientational order into account.

The model predicts that the CA transition is 2nd order in agreement with the continuous variation of the tilt angle at the transition as is the case for example in TBBA [21]. There are indications that first order CA transitions do occur as well [22]. This may be incorporated in the model by a coupling between the tilt and orientational order, but we did not study this possibility.

The CA phase transition in our model is not of the usual order-disorder type. It is driven by the variation in the entropy of packing. The contribution of this entropy is introduced in a somewhat \textit{ad hoc} manner. More experimental and theoretical work is necessary to clarify the precise role of packing.

The rotation about the long axes is assumed to be completely free. In order to explain the ferroelectricity in the chiral smectic C one must also consider terms which are capable of producing a minute rotational bias [23]. These terms can originate from induction forces as well.

A paper with more results and details is in preparation.

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