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The inplane local order of dipoles in the smectic B phases

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Résumé. — Dans cet article nous envisageons l'influence des répulsions stériques entre molécules d'un même plan smectique B sur l'ordre local des dipôles moléculaires. On calcule le facteur de corrélation diélectrique $G_{\perp}$ en développant une méthode qui permet de traiter les corrélations correspondantes au niveau d'approximation d'Ornstein-Zernike. Nous avons choisi un modèle simple de saut à six puits, compatible avec les résultats de Rayons X. Il en résulte une tendance à un ordre local de type ferroélectrique ($G_{\perp} > 1$) en accord avec la diminution expérimentale de l'anisotropie diélectrique en phase smectique.

Abstract. — In this paper we investigate the influence of steric repulsions between molecules within a smectic B plane, on the local order of molecular dipoles. We calculate the correlation factor $G_{\perp}$ and present a method which enables us to take into account the correlations of steric origin within the framework of the Ornstein-Zernike approximation. We have used a six well potential model compatible with the X-ray results. A local ferroelectric tendency results ($G_{\perp} > 1$) which is in accordance with the observed decrease of the dielectric anisotropy in the smectic phases.

1. Introduction. — In the smectic B (SmB) phases, tilted or not, the molecules are arranged in two dimensional hexagonal (or almost hexagonal) arrays; the molecules undergo orientational jumps around their long axis [1, 2, 3]. In X-ray and neutron experiments, especially performed on T.B.B.A., Levelut *et al.* [4, 5] have shown that the molecules rotate probably by $\pi/3$ orientational jumps and that the phenyl rings arrange themselves locally in a herring-bone type packing. Besides, this local order shows only a slight temperature dependence. In an earlier calculation [6] of the static susceptibility $\overline{\chi}(\mathbf{q})$ we have shown that this local order which expands in the smectic planes can properly be explained through the steric hindrance between phenyl rings of neighbouring molecules.

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Recent experiments [7] have shown that the dielectric behaviour in the smectic phases is very different from that in the nematic phase. It is characterized by a decrease of the dielectric anisotropy $\varepsilon_{\parallel} - \varepsilon_{\perp}$ as one proceeds to the more ordered liquid crystal phases. It may become negative in the SmB phase (EMBAC [8]). This seems to reflect a tendency of the parallel components of the molecular dipoles to form antiferroelectric local ordering and of the perpendicular components to arrange themselves locally in a ferroelectric local order. It has been ascribed to intermolecular correlations induced by the dipole-dipole interaction; calculations have been performed by de Jeu *et al.* [9] and later by Benguigui [8, 10].

The local order observed through X-ray and neutron scattering is that of the atoms which compose the molecule. It is mainly due to the phenyl rings which have an important transversal extension. The molecular dipoles are not directly connected with the phenyl rings and only an effect is expected for dipoles in the bridging group. The relative arrangement is not obvious, especially where NMR experiments [1] have shown that the molecules do not seem to be rigid and can change their conformation. But the $-\text{CH}=\text{NC}$ bonds of the T.B.B.A. molecule undergo rotations as well [11]. Then the rotational freedom of the phenyl rings is certainly dependent on the motion of the other parts of the molecule.

In this paper we argue that, apart from possible dipolar interactions, the steric repulsions which have an obvious effect on the local order detected by X-rays, affect the local order of dipoles as well. We attempt to evaluate the influence of the inplane molecular repulsions on the dielectric constant $\varepsilon_{\perp}$ of the SmB phases. This is done through the evaluation of the correlation factor $G_{\perp}$ using a simple model consistent with the X-rays [5] and NQR [11] results.

2. Model and calculation method. — We assume that the SmB phase is isotropic within the layer and that the molecules are at the sites of a plane hexagonal lattice. Within the framework of our model the molecule can assume six orientations around its long axis which, for simplicity are along the sides of the hexagonal lattice. We do not consider the rotation around the short molecular axis which is connected with the variation of $\varepsilon_{\parallel}$ and we assume that two neighbouring molecules within a plane would overlap with each other if they should get along the same side

Fig. 1. — The model of disorder in the smectic B plane. The arrows represent the six possible orientations. An example of steric incompatibility between the molecules at site 0 and 1 is shown.

(Fig. 1). If we suppose that in each molecule the perpendicular component of the molecular dipole makes a constant angle with the phenyl rings, it is easily checked that the dipolar correlations induced by the repulsion between the phenyl rings are independent of this angle. So the projection on the plane of the dipolar axis and of the benzene ring can be blended in our model representation of figure 1.

Let $\mathbf{E} = E \cdot \mathbf{e}$ be an electric field parallel to the plane, then the inplane polarization is :

$$P = \left\langle \sum_{i=0}^{N-1} \mu_i \cdot \mathbf{e} \right\rangle_{\{S\}} = Z_N^{-1} \sum_{\{S\}} \sum_{i=0}^{N-1} \mu_i \cdot \mathbf{e} \exp\left(\beta \mathbf{E} \cdot \sum_i \mu_i\right) \exp(-\beta U_{\{S\}}^{\text{Conf}}) \\ = \frac{1}{\beta} \frac{\partial \text{Log } Z_N}{\partial E} \quad (1)$$

where μ_i is the projection on the plane of the dipole of molecule i ($i = 0, N - 1$); $U_{\{S\}}^{\text{Conf}}$ is the configurational energy of the bi-dimensional crystal in the particular orientational configuration $\{S\}$; $Z_N = (Z)^N$ is the corresponding configurational partition function while $\beta = 1/kT$. The susceptibility in zero-field reads :

$$\left(\frac{\partial P}{\partial E} \right)_{E=0} = \beta \left\{ \left\langle \left[\sum_i (\mu_i \cdot \mathbf{e}) \right]^2 \right\rangle - \left[\left\langle \sum_i (\mu_i \cdot \mathbf{e}) \right\rangle \right]^2 \right\}_{E=0}. \quad (2)$$

In the rotator phase, the last term is zero in the zero-field limit, and for a N sites (N large) isotropic bi-dimensional system we get :

$$\left(\frac{\partial P}{\partial E} \right)_{E=0} = \frac{N\beta}{2} \sum_i \langle \mu_o \cdot \mu_i \rangle = \frac{N\beta}{2} G_{\perp} \langle \mu^2 \rangle. \quad (3)$$

The last equation defines an inplane correlation factor $G_{\perp}$ in which the correlations are summed over all molecules in the system. $G_{\perp}$ can be directly derived from an evaluation of Z_N as has been done in [13, 14]. It is equal to the Kirkwood factor $g_{\perp}$ if the correlations outside a large Kirkwood sphere decay rapidly enough [13].

On the other hand the definition of the expectation value of the projection of one particular dipole gives :

$$\left(\frac{\partial \langle \mu_o \cdot \mathbf{e} \rangle}{\partial E} \right)_{E=0} = \beta \left\{ \sum_i \langle (\mu_o \cdot \mathbf{e}) (\mu_i \cdot \mathbf{e}) \rangle - \langle \mu_o \cdot \mathbf{e} \rangle \left\langle \sum_i \mu_i \cdot \mathbf{e} \right\rangle \right\}_{E=0} \\ = \frac{\beta}{2} \sum_i \langle \mu_o \cdot \mu_i \rangle = \frac{\beta}{2} G_{\perp} \langle \mu^2 \rangle. \quad (4)$$

We shall make use of this last relation to calculate the influence of the steric hindrances on $G_{\perp}$. Our goal is a closed form evaluation at the Ornstein-Zernike (OZ) level of approximation. The problem at hand is not a straight enforcement of the mean field (M.F.) treatment currently used to study pretransitional effects : the involved energies are here far more important than kT_c [12].

Let us represent the orientation actually occupied by the j th molecule by a six component vector n^j such as

$$n_l^j = 1 \text{ if the molecular orientation at site } j \text{ is actually } l, \\ n_l^j = 0 \text{ if not,}$$

μ_l^j being the corresponding inplane projection of the molecular dipole. Its expectation value is given by :

$$\langle \mu_o \cdot \mathbf{e} \rangle = \sum_l (\mu_l^o \cdot \mathbf{e}) \langle n_l^o \rangle. \quad (5)$$

Considering that part of the interactions which directly relates to the hard core repulsions, we are concerned with a weighting factor which takes the form of a compatibility function $A(S_i S_j)$ taking either the value 1 or 0 depending of whether the molecular configurations S_i and S_j are sterically compatible or not. It is suitable to write [12, 13] :

$$A(S_i S_j) = 1 - C_{ij}(S_i) C_{ji}(S_j)$$

where $C_{ij}(S_i) = 1$ if the molecule i in the state S_i brings an arrow on ij
 $= 0$ if not.

Thus, in the presence of an electric field $\mathbf{E}$, we can write :

$$\langle n_l^o \rangle = Z_{N(E)}^{-1} \sum_{\{S\}} n_l^o \prod_{(ij)} A(S_i S_j) \prod_{i=1}^N \prod_{k=1}^6 (b_k^i)^{n_k^i} \quad (6)$$

where the first product runs over the edges (ij) of the plane lattice. b_k^i is the possible activity of the orientation k at the site i .

The system being isotropic in the plane we can choose for simplicity, the electric field to point along a symmetry axis (Fig. 1); so that in the presence of this electric field the statistical weights of the various orientations become :

$$b_1^o = b_2^o = e^L; \quad b_4^o = b_5^o = e^{-L}; \quad b_3^o = b_6^o = 1 \quad (L = \beta | \mathbf{E} \cdot \boldsymbol{\mu} |). \quad (7)$$

In the M.F. approximation, $A(S_i S_j)$ can be replaced by an effective one [12] :

$$\langle A(S_i S_j) \rangle_j = A_{ij}(S_i) = 1 - C_{ij}(S_i) \langle C_{ji}(S_j) \rangle \quad (8)$$

so that, for example :

$$A_{o1}(S_o = 1) = 1 - \langle n_4^1 \rangle; \quad A_{o1}(S_o \neq 1) = 1. \quad (9)$$

In the M.F. evaluation of (6), the summation is restricted to the states of the o molecule and the first product runs over the q neighbours of o only; thus the single particle partition function reads :

$$\begin{aligned} Z_{(E)}^{\text{M.F.}} &= \sum_{S_o} \prod_{(oj)} A_{oj}(S_o) \prod_{k=1}^6 (b_k^o)^{n_k^o} \\ &= (2 - \langle n_4^1 \rangle - \langle n_5^2 \rangle) e^L + (2 - \langle n_1^4 \rangle - \langle n_2^5 \rangle) e^{-L} + (2 - \langle n_6^3 \rangle - \langle n_2^5 \rangle). \end{aligned} \quad (10)$$

When writing the different $\langle n_l^o \rangle$ we get a set of consistency equations of the following form :

$$\langle n_1^o \rangle = [Z_{(E)}^{\text{M.F.}}]^{-1} (1 - \langle n_4^1 \rangle) e^L. \quad (11)$$

The self consistency of the system requires that $\langle n_l^o \rangle = \langle n_l^i \rangle \forall i, l$.

So that, in terms of the following variables ($\langle n_1^o \rangle = \langle n_2^o \rangle = x^+$, $\langle n_4^o \rangle = \langle n_5^o \rangle = x^-$, $\langle n_3^o \rangle = \langle n_6^o \rangle = x^o$) the set reduces to

$$\begin{aligned} x^+ &= [Z_{(E)}^{\text{M.F.}}]^{-1} (1 - x^-) e^L \\ x^- &= [Z_{(E)}^{\text{M.F.}}]^{-1} (1 - x^+) e^{-L} \\ x^o &= [Z_{(E)}^{\text{M.F.}}]^{-1} (1 - x^o). \end{aligned} \quad (12)$$

In the limit where $E \rightarrow 0$ ($L \rightarrow 0$) we get :

$$x^+ = \frac{1}{6} + \Delta^+; \quad x^- = \frac{1}{6} + \Delta^-; \quad x^0 = \frac{1}{6} + \Delta^0; \quad e^L = 1 + L$$

and (12) can be solved in term of first order perturbations :

$$\Delta^0 = 0; \quad \Delta^+ = -\Delta^- = \frac{5L}{24}.$$

This leads to :

$$\left(\frac{\partial \langle n_l^0 \rangle}{\partial L} \right)_{L=0} = \left(\frac{5}{24} \text{ if } l = 1, 2 \right) = \left(-\frac{5}{24} \text{ if } l = 4, 5 \right) = (0 \text{ if } l = 3, 6)$$

$G_{\perp}$ can be deduced from (4) and (5)

$$G_{\perp} = \frac{2}{\beta \langle \mu^2 \rangle} \sum_{i=1}^6 (\mu_i \cdot e) \left(\frac{\partial \langle n_l^0 \rangle}{\partial L} \right)_{L=0} \left(\frac{\partial L}{\partial E} \right)$$

owing to $L = \beta \mu E \cos \theta$ ($\cos \theta = \sqrt{3/2}$) one can easily check that :

$$G_{\perp} = \frac{30}{24} = 1.25.$$

Within the framework of the simple model that we have described here — a model which is compatible both with X-ray and NQR results — the steric restrictions between rotating molecules within the same layer give rise to an inplane local order of the dipoles showing a ferroelectric tendency ($G_{\perp} > 1$). This contributes to an enhancement of $\varepsilon_{\perp}$, which is in accordance with the experimental behaviour [8, 9]. The herring-bone local order observed in SmB phases through X-rays, experimentally appears as a gathering of the scattering (then of $\chi(\mathbf{q})$) around $\mathbf{q} = (2, 1, 0)$ ($|q| \neq 0$) [5]. The dielectric experiments are observed in $q = 0$; so one cannot expect that the invoked local order gives rise in this point to a considerable variation of the electric susceptibility. Moreover if a very precise calculation of $\chi(\mathbf{q})$ is necessary in the $\mathbf{q}$ -zone where it diverges [5], the level of approximation (OZ) that we use here is sufficient. The method we have presented here could be useful to study simultaneously and at the same level of approximation interactions of very different energy level such as the dipolar interactions and the steric repulsions.

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