Molecular theory of the ferroelectric and antiferroelectric phases in smectic liquid crystals

Anatoli A.Muravski[1], Frank Schmauder[1], Alfons Geiger[2] and Anatoli A.Minko[1]

[1]Institute of Applied Physical Problems, Minsk, Belarus
[2]Physical Chemistry, University of Dortmund, Germany

ABSTRACT

Molecular theory of the ferroelectric and antiferroelectric smectic phases is developed taking into account the distribution of dipole moment in molecule of liquid crystal. Very important role are played mutual dislocation different fragments molecules inside smectic layer and play key role in dipole-dipole interaction between neighbouring layers. Microscopic theory is constructed using the dipole-dipole interaction of the permanent molecular dipole moments. Three ordered phases are found, one has synclinic, second is anticlinic and third is twisted structure. In twisted structure the angle between two layers is 90 degree. Discuss specific ordering which is necessary for formation every phase.

Keywords: Ferroelectric, antiferroelectric, liquid crystal, molecular theory.

1. INTRODUCTION

Intensive investigations of smectic liquid crystals have started from the discovery of the surface-stabilized ferroelectric liquid crystal structure (SSFLC)[1,2]. First theoretical models for the smectic phase appeared 10 years before[3,4]. After these works much other experimental and theoretical researches were carried out, which investigated different aspects of the smectic phase. The short description of these works is possible to find in books[5,6,7].

The more important aspect all these investigations was to give an adequate description the structure of smectic layers and the mechanism of interaction between these layers. According to research results we can indicate four the most important moments characterizing smectic phase:

- All molecules in the smectic phase are localized in the periodical layer structure. Inside each layer the molecules are oriented parallel one another and can be tilted on some angle to the normal to this layer.
- Spontaneous polarization, existed in the smectic layer, is parallel to the plane of the inclined molecules in antiferroelectric phase SmC^*_A and is normal in ferroelectric phase SmC^*.
- Smectic layers with tilted molecules can form the helical structure in space.
- Dipole-dipole interactions between smectic layers play very important role in the formation of the mutual orientations these layers.

As was shown in[8,9,10] the energy of dipole-dipole interactions between two homogeneous polar planes equals to zero. Other words, such planes do not interact one to other. The interaction between dipole moments from neighbouring smectic layers is possible only between unaveraged dipole moments or between orientation fluctuations of the dipole moments. In[10] it was showing what short-range interaction between dipole moments from adjusted layers can stabilize anticlinic structure in neighbouring layers. For realization such mechanism the distance between dipole moments must be close to the distance between molecules inside smectic layers. But it is not possible. We propose the model of interaction between smectic layers that is based on the specific distribution of the dipole moments inside smectic layers, which follow from localization of the dipole moments in molecules and the ordering of these molecules inside smectic layers. For determination of the distribution of the molecular fragments, which has maximal dipole moment, inside smectic layers we have used the result of the molecular dynamics simulations MHPOBC in the periodic boundary conditions[11].

2. INTERACTION BETWEEN THE DIPOLE MOMENTS LOCATED IN NEIGHBOURING PLANES.

Take two polar planes with equal number of dipoles in each. Dipole moments located in one plane are μ_1 and located into other are μ_2. The energy of the interaction between two dipoles (μ_1 and μ_2), located at the distance $\mathbf{r}_{12}$, is determined in the following way

$$V_{12} = \frac{1}{r_{12}^3} \left[\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \vec{u}_{12})(\vec{\mu}_2 \cdot \vec{u}_{12}) \right] \tag{1}$$

where $\vec{u}_{12} = \dfrac{\vec{r}_{12}}{|r_{12}|}$ is the unit vector in direction from the first dipole to the second dipole.

If we have two uniformly oriented polar layers, there is no interaction between these layers [8,9,10]. But there exist specific interactions, which are caused by the orientation fluctuations of the dipole moments.

Let's consider dipole-dipole interaction inside one layer. Take the energy interaction of one dipole with all others from this layer equaled to $U(\theta)$, where θ is the angle between this dipole moment and the average dipole moment in the layer. The distribution function is then:

$$f(\theta) = A \cdot \exp\left(-\frac{U(\theta)}{kT} \right) \qquad \text{where} \qquad A = \left(\int_{-\pi}^{\pi} \exp\left(-\frac{U(\theta)}{kT} \right) d\theta \right)^{-1} \tag{2}$$

With this distribution function two-dimensional order parameters P_1 and P_2 is:

$$P_1 = A \int_{-\pi}^{\pi} \cos\theta \cdot f(\theta) d\theta \qquad P_2 = A \int_{-\pi}^{\pi} \left(2\cos^2(\theta) - 1 \right) \cdot f(\theta) d\theta \tag{3}$$

When we calculate the interaction between dipole from different layers we will take in account interaction with the nearest dipole and the homogenous layers without this dipole. In this case dipole-dipole interaction between two layers (calculated for one dipole) is:

$$U(\theta_2, \theta_1) = \frac{1}{r_{12}^3} \left[(\vec{\mu}_1 - \vec{\mu}_{1av}) \cdot (\vec{\mu}_2 - \vec{\mu}_{2av}) \right] =$$

$$\frac{|\mu|^2}{r^3} \left[\cos(\theta_2 - \theta_1 + \varphi) - P_1 \left(\cos(\theta_2 + \varphi) + \cos(\theta_1 - \varphi) \right) + P_1^2 \cos\varphi \right] \tag{4}$$

where θ_1 and θ_2 is the deviation angles to the average direction in layer, φ is angle between directions of average dipole moments alignment of in neighbouring layers (Fig. 1).
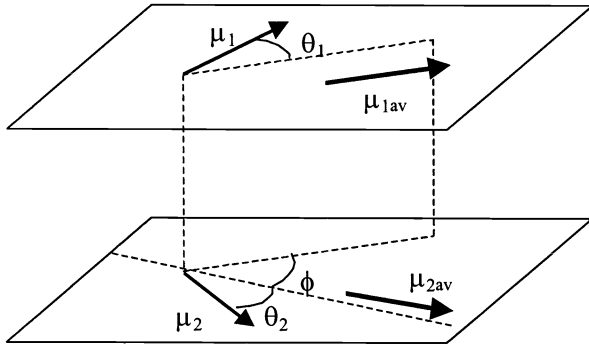

Figure 1. Mutual dislocation of dipole moments in neighbouring layers.

The energy interaction of the two polar planes in this case is

$$U = U(\theta_1) + U(\theta_2) + U(\theta_2, \theta_1) \tag{5}$$

Energy interaction between layers is small and we can use approximation

$$\exp\left\{ -\frac{U(\theta_2, \theta_1)}{kT} \right\} = 1 - \frac{U(\theta_2, \theta_1)}{kT}$$

and distribution function is next

$$f(\theta_1, \theta_2) = B \exp\left\{ -\frac{U(\theta_1) + U(\theta_2) + U(\theta_2, \theta_1)}{kT} \right\}$$

$$B = \left(\int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \exp\left\{ -\frac{U(\theta_1) + U(\theta_2) + U(\theta_2, \theta_1)}{kT} \right\} d\theta_1 d\theta_2 \right)^{-1} \tag{6}$$

and energy of interaction is:

$$U_{12}(\varphi) = B \int\limits_{-\pi}^{\pi} \int\limits_{-\pi}^{\pi} U(\theta_2, \theta_1) \exp\left[- \frac{U(\theta_1) + U(\theta_2) + U(\theta_2, \theta_1)}{kT} \right] d\theta_1 d\theta_2 =$$

$$B \int\limits_{-\pi}^{\pi} \int\limits_{-\pi}^{\pi} U(\theta_2, \theta_1) \left(1 - \frac{U(\theta_2, \theta_1)}{kT} \right) \exp\left[- \frac{U(\theta_1) + U(\theta_2)}{kT} \right] d\theta_1 d\theta_2$$

(7)

After the substitution the expression (4) into (7) and with (3) the interaction between two layers is next

$$U_{12}(\varphi) = - \frac{(d_a d_b)^2}{r^6 kT} (1 + P_{1a} P_{1b} \cos\varphi) \times$$

$$\times \left[\frac{1}{2}(1 - P_{2a} P_{2b}) - P_{1a} P_{1b}\left(1 - \frac{1}{2}(P_{2a} + P_{2b})\right) + (P_{2a} - P_{1a} P_{1b})(P_{2b} - P_{1a} P_{1b}) \cos^2\varphi \right]$$

(8)

where the indexes **a** and **b** indicate that this parameter belongs to layer 1 and 2 correspondingly.
The expression obtained for the interaction energy of the polar planes has minimum, if the average orientation of the dipole moments of the layers is parallel.

3.   MODEL OF THE TILTED SMECTIC LAYERS.

For the description of the electrostatic interaction between two smectic layers a transverse dipole moment is not enough. The electrostatics of the molecules of any smectic liquid crystal has to be described by additional local longitudinal dipole moments, which compensate each another but are located in different parts of the molecule (Fig. 2). In common case, longitudinal dipole moments μ_2 and μ_3 can be different ($|\mu_1| \neq |\mu_2|$) and the molecule can to have no only transverse but and longitudinal dipole moment.
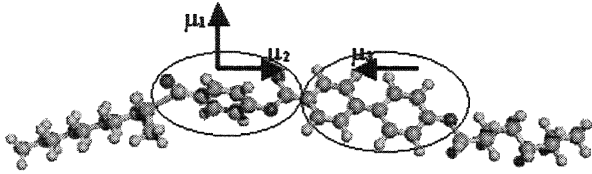

Figure 2.   Schematic position of local dipole moments in the
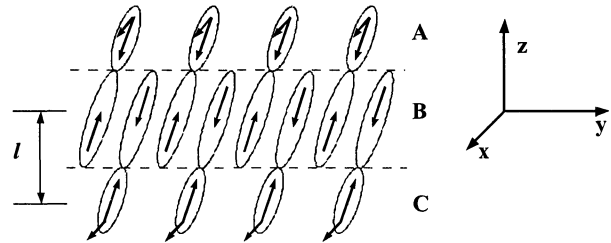molecule MHPOBC.

Figure 3.   Structure of a smectic layer. Division into sublayers.
The tilt is in the YZ-plane, the transverse dipole
moment in the X-direction.

When the molecules arrange themselves into smectic layers, these dipole moments form three sublayers. Every sublayer has its own average dipole moment and its own order of these dipole moments (Fig.3).

About the capability different fragments molecules form independent layers inside smectic layer was said in[12]. There was showed that the smectic layer has 3 independent layers: rigid, which is formed the rigid-rod parts of the molecules; flexible, which is formed aliphatic chains connected to rigid fragments; polar, which is formed by different polar fragments. Also it is possible different combination between these layers. In our model we show what a polar layer has own microstructure, which determinate the interlayer interaction in smectic liquid crystals.

Sublayers A and C have the same structure but the longitudinal dipole moments have opposite orientations. The sublayer B has a different structure. In this layer the longitudinal dipole moments are overlapping and completely compensating each other. In this case we can write the values for the parameters for every sublayers as given in Table 1.

Table 1. Parameters for every sublayers

	dipole moment $|\mu|$	Order parameter P_1
Sublayers A and C Projection of longitudinal d.m. on smectic layer plane	$\mu_{Ay} = \mu^o_{A\parallel} \cdot \sin\theta$	$P_{1\parallel} = \dfrac{P^o_{1\parallel} \cdot \sin\theta}{\sqrt{1 - P^{o\,2}_{1\parallel} \cos^2\theta}}$
Sublayers A and C Projection of transverse d.m. on smectic layer plane	$\mu_{Ax} = \mu^o_{A\perp}$	$P_{1\perp} = \dfrac{1}{2} \cdot \sin 2\theta$ Ref.[6]

θ is the tilt angle in the YZ-plane.

$\mu^o_{A\parallel}$ and $\mu^o_{A\perp}$ are the local dipole moments parallel and perpendicular to the molecular axis.

μ_{Ax} and μ_{Ay} are components of this local dipole moments in the plane of the sublayer A.

$P^o_{1\alpha} = \dfrac{\left|\langle \vec{\mu}_\alpha \rangle\right|}{\langle |\vec{\mu}_\alpha| \rangle}$, where μ_α ($\alpha = \perp, \parallel$) are the dipoles moments longitudinal and perpendicular to the molecular axis.

$P_{1\alpha}$ are the order parameters for the projections of these dipole moment components onto the smectic layer plane.
Localization of the sublayers can be determined from X-Ray analysis smectic structure or from result computer simulations. For MHPOBC we determined for the thickness of the sublayers A and C l=0.25d (d is thickness of the smectic layer). In this case the interaction between neighbouring sublayers from different layers will be an order of magnitude bigger then the interaction between other sublayers from different smectic layers. For our calculations we will consider only the interaction between these nearest sublayers (A and C from neighbouring smectic layers).

$$U(\varphi) = U_{\parallel,\parallel}(\varphi) + U_{\perp,\perp}(\varphi) + U_{\parallel,\perp}(\varphi) + U_{\perp,\parallel}(\varphi) \tag{9}$$

In formula (1) take that interaction between two sublayers A and C from different smectic layers is summa interactions between planes of the longitudinal and transverse dipole moments. If develop expression for interaction two dipole moments we received two parts: one for projection dipole moments on smectic layer and second for projection perpendicular to smectic layer. If we rotated one smectic layer relation to other second parts will not change. What why we can use for calculation interaction between two layers the formula for interaction two polar pane and use as dipole moments in this plane projection longitudinal and transverse dipole moments on plane smectic layer.
The energy of interaction between two polar planes can be written as (eq. 8)

$$U_{ab}(\varphi) = -\frac{(\mu_a \mu_b)^2}{r^6 kT}\left(1 + P_{1a}P_{1b}\cos\varphi\right) \times$$
$$\times\left[\frac{1}{2}(1 - P_{2a}P_{2b}) - P_{1a}P_{1b}\left(1 - \frac{1}{2}(P_{2a} + P_{2b})\right) + (P_{2a} - P_{1a}P_{1b})(P_{2b} - P_{1a}P_{1b})\cos^2\varphi\right] \tag{10}$$

where $r = d - 2 \cdot l$ for the sublayer interacted, φ is angle between directions of average dipole moments alignment of in neighbouring layers (Fig. 1), a and b are the projection of the longitudinal and transverse components of sublayers.

Depending on the relation between the magnitudes of the longitudinal and transverse dipole moments and the order parameters (P_1, P_2) we obtain an energy minima. There basic configurations of the layers: synclinic, anticlinic and twisted, with twist angles θ of 0, 180 and 90 degree. For each of these configurations there exists one energy minima for the mutual orientation φ of the smectic layers (Fig.3). The curves on this picture were received from equation 10 for the following parameters:
synclinic - $\mu^o_\perp / \mu^o_\parallel = 2$, $P^o_{1\parallel} = 0.7$, $P^o_{2\parallel} = 1$, $P_{1\perp} = 0.5$, $P_{2\perp} = 0.25$,
anticlinic - $\mu^o_\perp / \mu^o_\parallel = 0.25$, $P^o_{1\parallel} = 0.7$, $P^o_{2\parallel} = 1$, $P_{1\perp} = 0.5$, $P_{2\perp} = 0.25$,

twisted - $\mu^\circ_\perp / \mu^\circ_\parallel = 0.5$, $P^\circ_{1\parallel} = 0.7$, $P^\circ_{2\parallel} = 1$, $P_{1\perp} = 0.5$, $P_{2\perp} = 1$,
tilt angle $\theta = 30^\circ$ in all these cases.

Here symbol $< ^\circ >$ show what this parameter is determinate for longitudinal or transverse dipole moment of the molecule and recalculated with formula in Table 1; parameter without symbol $< ^\circ >$ is determinate for projection of the longitudinal or transverse dipole moment on plane smectic layer and is used directly in formula 10.

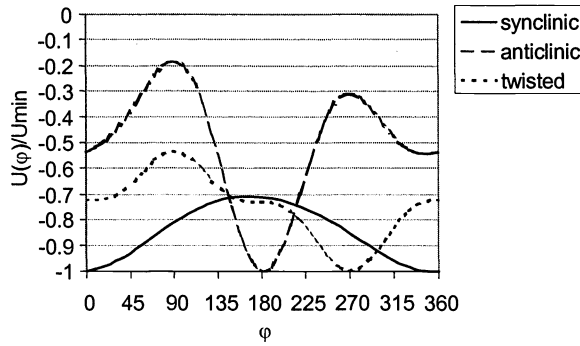Figure 4. Interaction between neighbouring layers in dependence of their mutual orientation for basic structure.
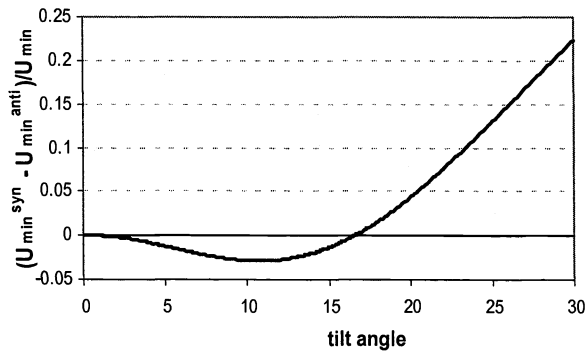
All other structures can be interpolated by the combination these structures, when some two are equiprobable, or modification these basic structure, when change relation between parameters of the system. In Figure 4 we can see what the symmetry of the curves in points of minimums is broken and point of minimums are a little shifted. This shift determinate the helical structure for the basic structure of the smectic crystal.

If tilt angle is changed then it is changed the relation between parameters of the system (see Table) and we can see the transition from one state to other. In Figure 5 there are displayed the relative difference of the energy minima in the synclinic and anticlinic structure in dependence by the tilt angle $\left(U^{syn}_{min} - U^{anti}_{min}\right)/U_{min}$, where U_{min} is minimal from these two values $U_{min} = min\left(U^{syn}_{min}, U^{anti}_{min}\right)$

Figure 5. Difference of the energy in the synclinic and anticlinic configuration in dependence of the tilt angle. $(\mu^\circ_\perp / \mu^\circ_\parallel = 0.5$, $P^\circ_{1\parallel} = 0.7$, $P_{2\parallel} = 1$, $P_{1\perp} = 0.5 \cdot sin2\theta$ [see ref.[6]], $P_{2\perp} = P_{1\perp}^2)$, φ correspond to the positions of the minima.
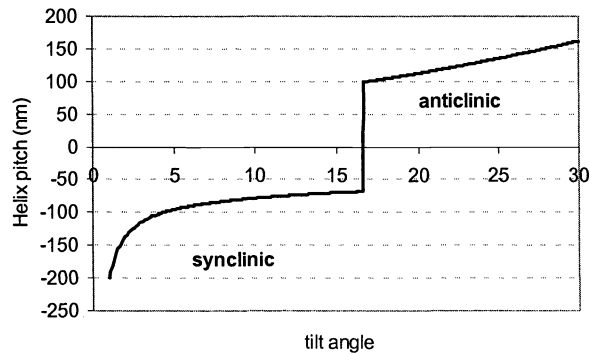
Figure 6. Helical pitch in dependence of the tilt angle. $(\mu^\circ_\perp / \mu^\circ_\parallel = 0.5$, $P^\circ_{1\parallel} = 0.7$, $P_{2\parallel} = 1$, $P_{1\perp} = 0.5 \cdot sin2\theta$ [see ref.[6]], $P_{2\perp} = P_{1\perp}^2)$. Here we use values $d = 3.0$ nm, $l = 0.75$ nm.

When this difference is equal zero it correspond the transition from anticlinic to synclinic configuration. In this moment in liquid crystal we can see inversion of the helix handedness (Fig.6). This effect was observed in experiment[13].

In point transition the helical pitch has sudden change not only of sign but also of the magnitude of pitch. Similar change was observed for MHFPDBC as function of temperature in [14].

Synclinic configuration exist when transverse dipole moment is bigger enough them projection longitudinal dipole moment on plane of the layer. If this condition is broken, system passes to the anticlinic configuration. Near point transition can exist twisted structure. For it is necessary next condition $P_{1\perp}^2 \ll P_{2\perp}$. It is possible if molecule has more that one local transverse dipole moment in the sublayer region and these dipole moments have possibility to rotate one relation to other. Such phase has name SmC_{FI2} and can be observed in much compound, for example 10OTBBB1M7, which has SmC_{FI2} phase in temperature range from $114^\circ C$ to $119.2^\circ C$ [15]. This compound has three transverse groups which has transverse dipole moments.
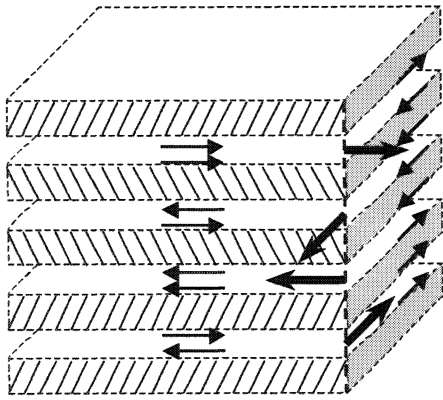
Figure 7. Structure of the dipole moment distribution in AF phase.

Near the point transition can exist structure which is result interaction the over layer polar planes. Example such structure can be AF phase [7]. Picture is explained the formation this structure displayed on Fig.6. This phase can exist only when synclinic and anticlinic structures have equal energy. In this time average dipole moment in the inter layering space form polar plane. This plane can interact and form twisted structure. For twisted structure must be performed condition $P_{1\perp}^2 \ll P_{2\perp}$, where perpendicular direction we can understand how direction perpendicular no compensate dipole moment for two adjusted sublayers. For dipole moments oriented in this direction order parameters $P_{1\perp} = 0$ but $P_{2\perp} \neq 0$ and it is the condition for formation twisted structure.

4. CONCLUSION

The presented model smectic liquid crystals consider only dipole-dipole interaction. Therefore this model gives description liquid crystals with big spontaneous polarization (molecules has big dipole moments in the molecules). We specially no used steric interaction to show effect dipole-dipole interaction in clean view. Our model show what practically all phase in tilted smectic liquid crystals are determined dipole-dipole interaction, whereas steric interaction determined the formation smectic layers and tilt of the molecules into layers.

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