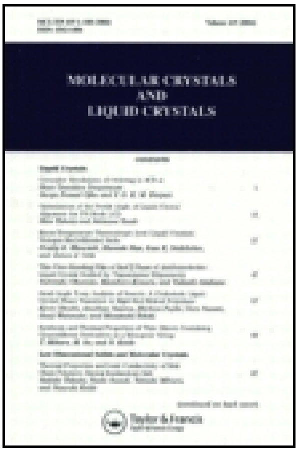

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Mojca Čepič [a] [b] & Boštjan Žekš [a] [c]

[a] J. Stefan Institute, Jamova 39, 1111, Ljubljana, Slovenia

[b] Faculty of Education, Kardeljeva pl. 16, 1113, Ljubljana, Slovenia

[c] Institute of Biophysics, Medical Faculty, Lipičeva 2, 1105, Ljubljana, Slovenia

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ELECTROSTATIC INTERLAYER INTERACTIONS IN TILTED POLAR SMECTIC LIQUID CRYSTALS

MOJCA ČEPIČ[†°] and BOŠTJAN ŽEKŠ[†*]
[†] J. Stefan Institute, Jamova 39, 1111 Ljubljana, Slovenia
[°] Faculty of Education, Kardeljeva pl. 16, 1113 Ljubljana, Slovenia
[*] Institute of Biophysics, Medical Faculty, Lipičeva 2, 1105 Ljubljana, Slovenia

Abstract

In chiral tilted smectic phases transverse molecular dipoles within a smectic layer order polarly as well as quadrupolarly. Electrostatic dipolar and quadrupolar interactions vanish between two smectic layers without positional correlations of molecules and exist only when the positions of molecules in the two layers are correlated. Therefore the interlayer electrostatic interactions are of short range and are expected to act only between nearest and next nearest layers. Dipolar interactions prefer antiferroelectric ordering of the tilt vectors in the two layers, while the quadrupolar interactions favour to have the tilt vectors in the two layers in two perpendicular directions.

INTRODUCTION

Antiferroelectric liquid crystals posses a large variety of different phases[1,2] with paraelectric, ferroelectric, antiferroelectric and ferrielectric properties, respectively. A phase with ferroelectric properties have been recognized as the normal Sm C* phase[3]. Antiferroelectric properties of the Sm C_A^* phase are the consequence of the oppositely tilted molecules in neighbouring layers[1]. For both structures also experimental evidences exist[4,5]. For the ferrielectric Sm C_γ^* phase and for the Sm C_α^* phase, which appears below the Sm A phase, different models have been proposed[6–9].

Recently, a new model based on interactions between nearest and next nearest layers, which is able to predict the experimentally consistent structures of different observed phases as well as different observed phase sequences in these materials, has been proposed[10]. Parameters of the model describe effective interactions between layers which are of steric, van der Waals and electrostatic origin. In this paper we shall discuss the dipolar and quadrupolar electrostatic interactions between nearest and next nearest smectic layers.

DIPOLAR INTERACTIONS

Each molecule, which is a constituent of an antiferroelectric liquid crystal, has a relatively large dipole moment. In tilted chiral phases, as for example the Sm C* phase, the molecule experiences hindered rotation and therefore posseses an average dipole moment. Due to the head and tail symmetry of molecular orientations in each layer exists a net dipole moment in a direction perpendicular to the smectic layer normal (z direction) and to the average molecular tilt. To the energy of electrostatic dipolar interactions between layers contributes only this component of the molecular dipole moment.

To evaluate electrostatic dipolar interactions between nearest and next nearest layers in tilted phases with dipole moments as discussed, we choose the following geometry:

- In the j-th layer molecules are tilted in x direction and the tilt vector in the j-th layer is $\vec{\xi}_j = \theta\{1, 0\}$, where θ is a magnitude of the tilt. The average dipole moment is perpendicular to the tilt vector in y direction or $\vec{p}_j = p_0\{0, 1\}$ and p_0 is an average molecular dipole moment.
- In the $(j+n)$-th layer molecules are tilted in a direction which has an angle α_n in respect with x-axes and tilt vector in this layer is $\vec{\xi}_{j+n} = \theta\{\cos\alpha_n, \sin\alpha_n\}$. The average dipole moment of the molecule is perpendicular to this direction, $\vec{p}_{j+n} = p_0\{-\sin\alpha_n, \cos\alpha_n\}$.
- The coordinate system has the origin in the center of mass of the first interacting molecule in the j-th layer, while center of mass of the second molecule from $(j+n)$-th layer is in the position $\vec{r} = \{x, y, nd\}$. We express $\vec{r}$ in polar coordinate system with origin in the center of mass of the first molecule in the j-th layer, $\vec{r} = \{\rho\cos\phi, \rho\sin\phi, nd\}$. Complete smectic order is assumed, therefore the z-th component is always nd for two molecules from j-th and $(j+n)$-th layer.

An electrostatic interaction of two molecules from j-th and $(j+n)$-th layers is than:

$$V_{d,n}(\rho,\phi) = \frac{p_0^2}{4\pi\epsilon_0}\,\frac{((nd)^2 + \frac{1}{2}\rho^2)\cos\alpha_n + \frac{3}{2}\rho^2\cos(\alpha_n - 2\phi)}{((nd)^2 + \rho^2)^{(\frac{5}{2})}}, \tag{1}$$

where index d stands for dipolar. From the expression (1) it is clearly seen that for $\phi = 0, \pi$, antiparallely tilted molecules ($\alpha_n = \pi$) are stable, whereas for $\phi = \pm\pi/2$, antiparallel tilts are stable for $\rho < 0.707(nd)$, while for larger distances the opposite is true ($\alpha_n = 0$). The electrostatic energy of interacting layers is a sum over all interacting molecules in both layers. As long as two layers can be treated as two dimensional liquids without any positional correlations between molecules, the corresponding sum i.e. integral can be expressed as[11]

$$V_d(j, j+n) = \tilde{p}^2 \int_{S_j, S_{j+n}} \rho_j d\rho_j \; d\phi_j \; \rho_{j+n} d\rho_{j+n} \; d\phi_{j+n} \; V_{d,n}(\rho_{j+n,j}, \phi_{j+n,j})/p_0^2 = 0. \qquad (2)$$

In the expression (2) $\tilde{p}$ is an average dipole moment for a unit of area, S_j, S_{j+n} are the areas of j-th and $(j+n)$-th smectic layers and $\rho_{j+n,j}, \phi_{j+n,j}$ are polar coordinates of the position in $(j+n)$-th layer in respect with the position in the j-th layer. It is clearly seen that layers do not interact. But we can expect that due to the incomplete smectic ordering and therefore molecular interpenetration through neighbouring layers, positions of molecules in nearest layers are correlated. We assume a simple positional correlation between interacting molecules in nearest and next nearest layers. In order to find the effective electrostatic dipolar interactions between nearest layers, we assume a following approximation of positional correlation between molecules of nearest layers: molecules from the j-th nearest layers i.e. $j+1, j-1$, approach to the molecule from the j-th layer due to the interpenetration only to its radius b. In the distance $2b$ centers of masses of six molecules can be found (see Figure 1). Correlations to larger distances within a smectic layer are neglected. The tilt dependence of positional correlations has not been analysed. For small tilts it is assumed to be the same as in the Sm A phase. The effective dipolar interaction of one molecule from j-th layer with molecules in nearest $(j+1)$-st layer is expressed as:

$$V_{d,1} = \frac{1}{2\pi} \int_0^{2\pi} d\phi \left[6V_{d,1}(2b, \phi) - \frac{6}{\pi(3b)^2} \int_0^{3b} V_{d,1}(\rho, \phi) \, \rho \, d\rho \right] = E_{d,1}(b) \, p_0^2 \, \cos\alpha_1, \qquad (3)$$

where d stands for dipolar, 1 for nearest layer and α_1 is the phase angle between tilts in nearest layers. The interacting energy is averaged over rotationally symmetric positions (ϕ), because there is no preferred direction within layers. The interacting energy with a two dimensional liquid in the same area is subtracted. The coefficient $6/\pi(3b)^2$ appears due to the conservation of mass in the smectic layer. The interacting energy $V_{d,1}$ depends on the phase difference between tilts α_1, molecular radius b, an

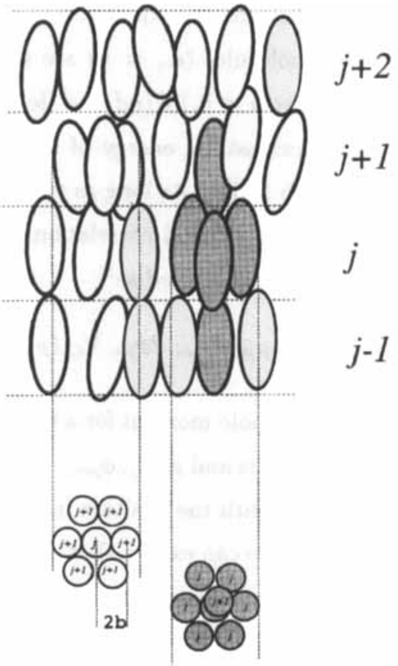
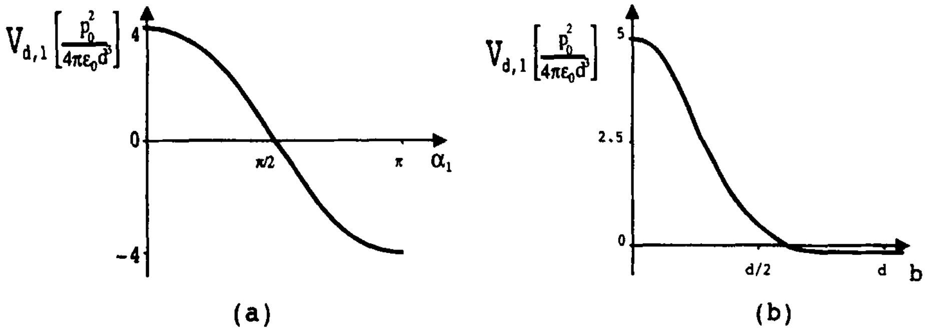


Figure 1: A side view and a projection on the smectic layer of interacting molecules from j-th, its nearest and next nearest layers.

average molecular dipole moment p_0 and interlayer distance d. It turns out that for elongated molecules, where $b < 0.641\ d$, effective dipolar interactions always favour antiparallel ordering ($\cos\alpha_1 = -1$ or $\alpha_1 = \pi$) of dipoles i.e. antiparallel tilt vectors in nearest layers (Figure 2 a,b), otherwise parallel orientation of molecular tilts or ferroelectric ordering is favoured (Figure 2 b).

Also positions of molecules in next nearest layers are correlated to some extent. It is more probable for a molecule from the next nearest layer, ($j+2$), to be found directly above the molecule from the j-th layer, since there exist a hole due to the absence of molecules from nearest layer (Figure 1). Correlations to larger distances within a smectic layer are neglected. The effective interaction of the molecule with



(a)

(b)

Figure 2: Dependence of interacting energy $V_{d,1}$ expressed in $p_0^2/(4\pi\epsilon_0 d^3)$ (a) of phase difference α_1 for elongated molecules where $b = 0.1\ d$ and (b) of the molecular radius b expressed in its length d for phase difference $\alpha_1 = 0$.

molecules in next nearest layers is therefore:

$$V_{d,2} = V_{d,2}(0,\phi) - \frac{1}{2\pi}\int_0^{2\pi} d\phi \left[\frac{6}{\pi(3b)^2}\int_0^{\sqrt{\frac{2}{3}}b} V_{d,2}(\rho,\phi)\ \rho\ d\rho\right] = E_{d,2}(b)\ p_0^2\ \cos\alpha_2, \tag{4}$$

where index d stands for dipolar, 2 for next nearest layer and α_2 is the phase angle of tilts in next nearest layers. Again, the interacting energy with two-dimensional liquid in the interacting area is subtracted and the integration limit $\sqrt{2/3}\ b$ appears due to the conservation of mass in smectic layer. The interacting energy $V_{d,2}$ depends on the phase difference between molecular tilts α_2, molecular radius b, an average dipole moment p_0 and interlayer distance d. It turns out that dipolar interactions always favour structures with tilt vectors in next nearest layers in the opposite directions i.e. $\cos\alpha_2 = -1$. The magnitude of dipolar interactions between next nearest layers for elongated molecules, which have radius ten times smaller than their length, presents in our approximation only 2 hundreds of dipolar interactions between nearest layers. Since dipolar interactions between nearest smectic layers can be canceled out by steric and van der Waals interactions, which favour parallelism of molecular tilts, the dipolar interactions between next nearest layers cannot be neglected in some cases.

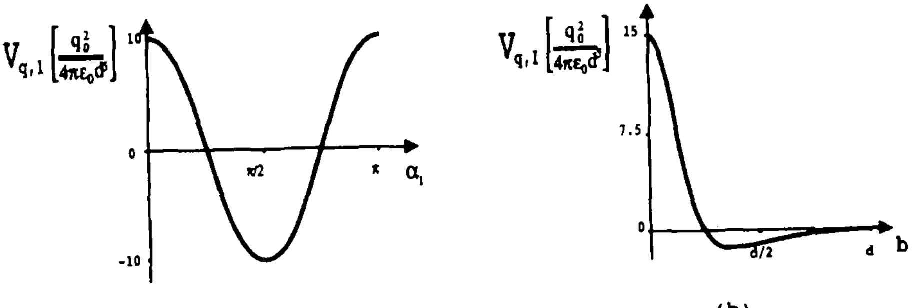
QUADRUPOLAR INTERACTIONS

Transverse molecular dipoles can be ordered also in a quadrupolar way. Such average molecular quadrupole moments can be quite large, especially when two dipoles are aranged in the opposite directions, like in MHPOBC [12]. Due to the hindered rotation of molecules, average positions of two oppositely oriented charges are approximated with following linear distribution of charges in a direction perpendicular to the direction of average dipole moment: two positive charges e^+ are a distance $2a_q$ apart and exactly in the middle is a negative charge $2e^-$. A quadrupole moment of the molecule is therefore $q_0 = ea_q^2$. The electrostatic quadrupole - quadrupole interacting energy of two molecules from the j-th and $(j+n)$-th layer is obtained as an expansion of electrostatic potential of interacting charges, arranged as described, in terms a_q. The expression is a good approximation of interacting potential providing $a_q << |r|$:

$$\begin{aligned} V_{q,n}(\rho,\phi) &= \frac{3}{8}\frac{q_0^2}{4\pi\epsilon_0}\cdot \\ &\cdot \left[\frac{(8(nd)^4 - 24(nd)^2\rho^2 + 3\rho^2)(2+\cos 2\alpha_n) + 35\rho^4\cos(2\alpha_n - 4\phi)}{((nd)^2+\rho^2)^{(\frac{9}{2})}} + \right. \\ &\left. + \frac{10\rho^2(6(nd)^2 - \rho^2)(\cos(2\alpha_n - 2\phi) + \cos 2\phi)}{((nd)^2+\rho^2)^{(\frac{9}{2})}}\right] \end{aligned} \tag{5}$$

where ρ, ϕ, α_n and (nd) were already defined for calculation of dipolar interactions. Similarly as for dipolar interactions, regions of different favourable orientations of dipoles exist. For example, directly above the molecule from the j-th layer or for $\phi = 0, \pi$ molecular tilt tends to be orieted perpendicularly to the direction of the molecular tilt in the j-th layer i.e. $\alpha_n = \pm\pi/2$. For $\phi = \pm\pi/2$ three regions exist: for $\rho < 0.362(nd)$ and $\rho > 1.694(nd)$ perpendicularly oriented molecular tilts are favoured, otherwise parallel or antiparallel orientation of molecular tilts is preferred. Again, an energy of quadrupolar interactions between two different layers can be calculated as a sum over all interacting molecules in two different layers. As long as there is no positional correlations of molecules in interacting layers i.e. they can be treated as two-dimensional liquids, the sum can be replaced by an integral of the form

$$V(j, j+n) = \tilde{q}^2 \int_{S_j, S_{j+n}} \rho_j d\rho_j \; d\phi_j \; \rho_{j+n} d\rho_{j+n} \; d\phi_{j+n} \; V_{q,n}(\rho_{j+n,j}, \phi_{j+n,j})/q_0^2 = 0. \tag{6}$$



(a) (b)

Figure 3: Dependence of interacting energy $V_{q,1}$ expressed in $q_0^2/(4\pi\epsilon_0 d^5)$ (a) of phase difference α_1 for elongated molecules where $b = 0.1\ d$ and (b) of the molecular radius b expressed in its length d for phase difference $\alpha_1 = 0$.

In the expression (6) $\tilde{q}$ is an average quadrupole moment for a unit of area and $S_j, S_{j+n}, \rho_{j+n,j}, \phi_{j+n,j}$ are defined as in (2). Again, as long as there is no positional correlations between molecules of two different layers, these two layers do not interact and similarly as before we expect interactions when at least some positional correlations between nearest and between next nearest layers exist. Quadrupolar interactions between more than two layers are negligible because there is nearly no positional correlations between molecules. Quadrupolar interactions between nearest and next nearest layers are calculated similarly as dipolar interactions in (3,4).

$$V_{q,1} = \frac{1}{2\pi}\int_0^{2\pi} d\phi\ \left[6V_{q,1}(2b,\phi) - \frac{6}{\pi(3b)^2}\int_0^{3b} V_{q,1}(\rho,\phi)\ \rho\ d\rho\right] = E_{q,1}(b)\ q_0^2\ \cos^2\alpha_1, \tag{7}$$

$$V_{q,2} = V_{q,2}(0,\phi) - \frac{1}{2\pi}\int_0^{2\pi} d\phi\ \left[\frac{6}{\pi(3b)^2}\int_0^{\sqrt{\frac{2}{3}}b} V_{q,2}(\rho,\phi)\ \rho\ d\rho\right] = E_{q,2}(b)\ q_0^2\ \cos^2\alpha_2, \tag{8}$$

where index q stands for quadrupolar, 1 is for nearest layers and 2 for next nearest layers interactions. Both interacting energies $V_{q,1}$ and $V_{q,2}$ are dependent of phase differences between tilts α_1 and α_2, respectively, molecular radius b, an average qudrupole moment q_0 and interlayer distance d. For elongated molecules where $b < 0.284\ d$, $E_{q,1}$ is positive (Figure 3 b). In this case minimum of interacting energy occurs when molecular tilts in neighbouring layers are oriented perpendicularly i.e. $\cos^2\alpha_1 = 0$ (Figure 3 a). For more spherical molecules parallel or antiparallel orientations are favoured or $\cos^2 \alpha_1 = 1$. For next nearest layers quadrupolar interactions $E_{q,2}$ is always positive and perpendicular orientations of tilts in next nearest layers is always favourable. For elongated molecules, which have radius ten times smaller than their length, the value of $E_{q,2}$ is at least for three orders of magnitude smaller than $E_{q,1}$. Since no interactions, which could cancel out favourable perpendicular oriented tilts between nearest layers exist, quadrupolar interactions between next nearest layers can be neglected.

CONCLUSIONS

We have shown that electrostatic dipolar and quadrupolar interactions exist between smectic layers only when there exist positional correlations between positions of molecules from interacting layers. A simple positional correlations between molecules from nearest and next nearest layers have been assumed and dipolar as well as quadrupolar electrostatic interactions up to the next nearest layers have been calculated.

Electrostatic dipolar interactions favour antiparallel orientation of molecules in interacting layers. In the case of prevailing dipolar interactions between nearest layers over other interactions, the double helix structure of the antiferroelectric Sm C_A^* phase[1] is stable. When interactions between nearest layers are comparable and compete with dominating dipolar next nearest layers interactions, a helicoidally modulated tilted structure of the Sm C_α^* phase[8,10] is stable. A helicoidal modulation extends over only few layers and is not of chiral origin. It appears due to the competition between nearest layers interactions, which favour parallel or antiparallel oriented tilt vectors in nearest layers, with dominating dipolar interactions between next nearest layers, which favour antiparallel orientations in next nearest layers. For elongated molecules with large quadrupole momentum quadrupolar interactions favour perpendicular oriented tilt vectors in interacting layers. When steric and van der Waals interactions cancel out the electrostatic dipolar interactions between nearest layers, and between next nearest layers van der Waals interactions, which prefer parallel ordering, are prevailing, quadrupolar interactions stabilize the structure where two ferroelectric helices gear into each other in general angle. Therefore these interactions stabilize the ferrielectric Sm C_γ^* phase[8-10].

Electrostatic interactions, which appear only in systems where some positional correlations of molecules in different smectic layers exist, can stabilize some of phases appearing in antiferroelectric liquid crystals. Tilt i.e. temperature dependence of positional correlations between molecules from interacting layers and therefore effective electrostatic interactions between layers result in a large variety of phases as well as their phase sequences. It seems that prevailing electrostatic interactions between smectic layers are the main origin of the most of phases appearing in antiferroelectric liquid crystals.

REFERENCES

1. A.D.L.Chandani, E. Gorecka, Y.Ouchi, H.Takezoe, A. Fukuda, Jpn.J.Appl.Phys., 28, 1265 (1989).
2. A. Fukuda, Y. Takanishi, T. Isozaki, K.Ishikawa, and H. Takezoe, J.Matter.Chem., 4, 997 (1994).
3. R.B. Meyer, L.Liebert, L. Strzelecky, P.Keller, J.Phys. (Paris) Lett., 36, L69 (1975).
4. Y. Galerne, L. Liebert, Phys. Rev. Lett, 66, 2891 (1991).
5. Ch. Bahr, D. Fliegner, Phys. Rev. Lett, 70, 1842 (1993).
6. T.Isozaki, K.Hiaroka, Y.Takanishi, H.Takezoe, A.Fukuda, Y.Suzuki, I.Kawamura, Liq.Cryst., 12,59 (1992); T.Isozaki, T.Fujikawa, H.Takezoe, A.Fukuda, T.Hagiwara, Y.Suzuki, I.Kawamura, Phys.Rev.B, 48, 13439 (1992).
7. H.Orihara, Y.Ishibashi, Jpn.J.Appl.Phys, 30, L1819 (1990); H.Sun, H. Orihara, Y. Ishibashi, J.Phys.Soc.Jap., 62, 2706 (1993).
8. B. Žekš, M. Čepič, Liq. Cryst., 14, 445 (1993); M. Čepič, B. Žekš, Mol. Cryst. Liq. Cryst., 263, 61, (1995).
9. V. Lorman, A.A. Bulbitch, P. Toledano, Phys. Rev. E, 49, 1367 (1994).
10. M. Čepič, B. Žekš, submitted to publication.
11. R. Bruinsma, J. Prost, J. Phys. II France, 4, 1209, (1994).
12. Y. Takanishi, K. Hiraoka, V.K. Agrawall, H. Takezoe, A. Fukuda, K. Terashima, Jap. J. App. Phys., 30, 2023, (1991).