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Antiphase structures in polar smectic liquid crystals and their molecular origin

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Abstract

We demonstrate that the overall molecular dipole organization in a smectic liquid crystal formed of polar molecules can be strongly influenced by the position of the dipole in the molecule. We study by large scale Monte Carlo simulations systems of attractive–repulsive "Gay–Berne" elongated ellipsoids with an axial dipole at the center or near the end of the molecule and we show that monolayer smectic liquid crystals and modulated antiferroelectric bilayer stripe domains similar to the experimentally observed "antiphase" structures are obtained in the two cases.

Liquid crystals are states of matter where the orientational order of the constituent molecules is coupled with a long range positional order that is reduced (in smectics) or absent (in nematics) compared to that of crystals [1]. A further classification of smectics is based on the presence of molecular tilt with respect to the layer (smectic C, S_C) or the residual long range positional order inside the layers which can be typically non-existent (smectic A, S_A), hexagonal (smectic B, S_B), etc. [2]. The situation is further complicated when molecules have specific electrostatic interactions, in particular permanent dipoles. Various types of structures have been experimentally found in smectic A liquid crystals formed by elongated polar molecules [1-3]. The dipoles can be randomly distributed inside each layer giving a monolayer structure (S_{A_1}) or paired anti-ferroelectrically forming a uniform bilayer (S_{A_2}) or a local bilayer with modulation of domains with up and down dipoles in the "antiphase" ($S_{\tilde{A}}$) structures [3].

Understanding the link between molecular structure and the resulting collective organization is of importance both from a fundamental and a technological point view, as a significant aid in guiding the design and synthesis of new materials. The problem is, however, extremely complicated since molecules forming mesophases are normally quite complex, with rigid aromatic or alternatively saturated cores, flexible chains and shape asymmetry as well as dipoles or quadrupoles [2]. The classical modelling and simulation approach working with atomistic or "united atoms" resolution, can be of help in studying local behaviour [4,5], but is limited by the number of molecules N it can consider (normally $N \lesssim 10^2$), while a large number of molecules (of the order of 10^3) is required to observe phase transitions and to reduce the effects of sample size. Moreover an atomistic simulation in its quest for realism simultaneously involves a number of contributions to the intermolecular interactions, making it difficult to disentangle the various contributing terms. On the other hand simulations performed at molecular resolution level with simple model potentials [6-9] can be important in trying to find a "minimal" set of molecular properties

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sufficient to produce a certain liquid crystal phase. Comparatively less has been done on polar liquid crystals [10,11], even though there is strong interest in understanding what molecular features determine the variety of smectics mentioned before and favour the formation of the predicted [12], but as yet unobserved, uniaxial ferroelectric phase. Part of the reason is computational. Dipolar forces are long range and the computer time required for their evaluation is more than linear in N (e.g. with the Ewald technique [13,14] it grows as $N^{3/2}$) so that the requirement of large N indicated before implies the use of massive amounts of computer time.

Here we make an attack on the problem and consider a fairly large system of uniaxial ellipsoidal particles of semiaxes σ_e and σ_s with an embedded electric dipole. The pair potential is the sum of a Gay–Berne (GB) [6,9] and a dipole–dipole term: $U^*_{ij} = U^*_{GB} + U^*_{dd}$. The Gay–Berne term has a repulsive and attractive contribution with a 12–6 inverse distance dependence form:

$$U^*_{GB}(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\boldsymbol{r}) = 4\epsilon_s\epsilon(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\hat{\boldsymbol{r}}) \times\left[\left\{\frac{\sigma_s}{r-\sigma(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\hat{\boldsymbol{r}})+\sigma_s}\right\}^{12} - \left\{\frac{\sigma_s}{r-\sigma(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\hat{\boldsymbol{r}})+\sigma_s}\right\}^{6}\right], \tag{1}$$

with unit vectors $\hat{\boldsymbol{u}}_i$, $\hat{\boldsymbol{u}}_j$ defining the orientation of the particles i and j; $\boldsymbol{r} = \boldsymbol{r}_j - \boldsymbol{r}_i \equiv r\hat{\boldsymbol{r}}$ the intermolecular vector of length r. The rather complicated anisotropic contact distance $\sigma(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\hat{\boldsymbol{r}})$ and interaction energy $\epsilon(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\hat{\boldsymbol{r}})$ are defined as in Ref. [6] and we employ the same parametrization used in Ref. [9], in particular: shape anisotropy $\sigma_e/\sigma_s = 3$, interaction anisotropy $\epsilon_s/\epsilon_e = 5$. σ_s and ϵ_s are used as molecular units of length and energy. The dipolar energy is given by

$$U^*_{dd} = \frac{\mu^*_i\mu^*_j}{r_d^3}\left[\hat{\boldsymbol{u}}_i\cdot\hat{\boldsymbol{u}}_j - 3(\hat{\boldsymbol{u}}_i\cdot\hat{\boldsymbol{r}}_d)(\hat{\boldsymbol{u}}_j\cdot\hat{\boldsymbol{r}}_d)\right], \tag{2}$$

where $\boldsymbol{r}_d \equiv \hat{\boldsymbol{r}}_d r_d$ is the vector joining the two point dipoles at distance r_d. We consider axial dipole moments $\boldsymbol{\mu}^*_i \equiv \mu^*\hat{\boldsymbol{u}}_i$, $\boldsymbol{\mu}^*_j \equiv \mu^*\hat{\boldsymbol{u}}_j$ (the dimensionless $\mu^* \equiv (\mu^2/\epsilon_s\sigma_s^3)^{1/2}$) positioned (a) in the center of the molecule or (b) shifted a distance $d^* \equiv d/\sigma_s = 1$ along the long molecular axis. In both cases two isolated molecules would arrange their dipoles antiparallel and without the use of computer simulations it is not feasible to predict what the resulting molecular and dipolar organization would be at a certain thermodynamic state point, although some approximate theoretical treatments exist [15].

We have performed extensive canonical ensemble (constant number of molecules N, volume V and temperature T) Monte Carlo (MC) simulations of a system of $N = 1000$ interacting particles enclosed in a cubic box with periodic boundary conditions at a reduced density $\rho^* \equiv N\sigma_s^3/V = 0.30$ and for three dimensionless temperatures $T^* \equiv kT/\epsilon_s = 4.0$, 3.4 and 2.0 corresponding to isotropic (I), nematic (N) and smectic (S_A) phases for the reference state in the absence of dipoles [9]. We use a reduced dipole moment $\mu^* = 2$ that, assuming a molecular cross section $\sigma_s = 5$ Å and an energy scale $\epsilon_s/k = 100$ K, would correspond to about 2.4 D, similar to that of a nitro group.

The dipolar energy for particles in the box surrounded by its periodic images has been computed using the Ewald sum technique [13,14] with convergence parameter $\alpha = 4.8$, and lattice vectors $\boldsymbol{n}$ with $n^2_{\max} = 6$ and largest individual component $n_{i,\max} = 2$ (notation of Ref. [14]) and tin foil boundary conditions, i.e. dielectric constant $\epsilon = \infty$ outside the simulation box. A satisfactory convergence of the Ewald sum is achieved with these values. The MC evolution takes place with single molecule updates as described in [16], but we have found essential to add dipole flip MC moves since, at least at low temperature, these are not likely to come about in a practical time if only small angular steps are used, with the danger of becoming locked in a metastable state. In practice we use two workstations working in parallel with PVM [17] to update the configurations and to compute the observables. Typical runs for the $N = 1000$ particles were started from dipole-less equilibrium configurations and equilibrated with dipole on for over 200000 cycles (N attempted moves) with production runs of 100–200000 cycles. We find that the three state points correspond to I, N and smectic even in the presence of dipolar forces and we summarize results in Table 1. We see that for the chosen dipole the stabilizing effect on the energy is important, especially for the shifted dipole, while the order parameter $\langle P_2\rangle = \langle 3\cos^2\beta - 1\rangle/2$ [16], with β angle between molecu-

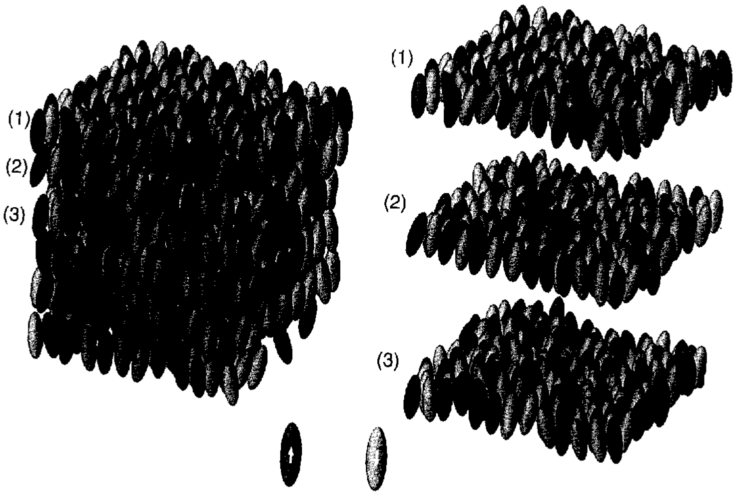

Fig. 1. The molecular organization in the smectic phase for the $N = 1000$ central dipole system in the smectic phase ($T^* = 2.0$). Dark and light gray molecules represent dipoles pointing up and down respectively. We show a three dimensional side view of the sample (left) and an exploded view of the first three layers (right).

Table 1
Results from MC simulation of $N = 1000$ systems of GB rod-like molecules either with no dipole or with axial dipole μ^* at the center or along the axis at distance d^* from the center. We report the energy $\langle U^* \rangle$, the order parameter $\langle P_2 \rangle$ [16] and the dielectric constant [13,14] $\bar{\epsilon} = 1 + 4\pi\rho^*(\langle \boldsymbol{M} \cdot \boldsymbol{M} \rangle - \langle \boldsymbol{M} \rangle \cdot \langle \boldsymbol{M} \rangle)/3NT^*$, where $\boldsymbol{M} \equiv \sum_{i=1}^{N} \boldsymbol{\mu}_i^*$ is the total dipole moment, at three reduced temperatures T^* corresponding to the phases indicated

T^*	μ^*	d^*	$\langle U^* \rangle$	$\langle P_2 \rangle$	$\bar{\epsilon}$	Phase
2.0	-	-	-10.4 ± 0.1	0.92 ± 0.01	-	S_A
	2.0	0.0	-13.9 ± 0.1	0.95 ± 0.01	1.2 ± 0.1	S_{B_1}
	2.0	1.0	-19.2 ± 0.1	0.97 ± 0.01	1.1 ± 0.1	$S_{\tilde{A}}$
3.4	-	-	-4.9 ± 0.2	0.63 ± 0.03	-	Nem
	2.0	0.0	-6.1 ± 0.2	0.67 ± 0.03	2.7 ± 0.2	Nem
	2.0	1.0	-8.1 ± 0.2	0.73 ± 0.02	2.2 ± 0.1	Nem
4.0	-	-	-2.0 ± 0.2	0.09 ± 0.04	-	Iso
	2.0	0.0	-2.9 ± 0.2	0.09 ± 0.03	2.1 ± 0.1	Iso
	2.0	1.0	-4.0 ± 0.2	0.11 ± 0.03	2.1 ± 0.1	Iso

lar axis and director is less affected. However useful, these scalar quantities are not very informative on the molecular organization we now concentrate on, which is actually strikingly different in the smectic (low temperature phase).

In Fig. 1 we show a configuration obtained for the smectic system with central dipole, showing that the dipoles have an essentially random anti-parallel orientation inside the smectic layer, with little correlation between layers. An examination of the radial distribution $g_0(r)$ (thick continuous curve in Fig. 2A) also shows that the central dipole smectic has a stronger nearest neighbour peak compared with the apolar system, indicating a stronger layering with little interdigitation (see Fig. 2D), consistent with the density distribution $g(z)$ in Fig. 2B, that has a wavelength only 7% lower than $2\sigma_e$. Moreover we see a behaviour typical of an hexagonal S_B type order in the position and intensity of the peaks, e.g. in the characteristic split of the second peak [9]. We could call this phase a monolayer S_{B_1}, in analogy with the S_{A_1} devoid of this hexagonal order.

The simulation of the shifted dipole system gives the very different dipole organization shown in Fig. 3. Here at short range the dipoles point in the same direction (same colour here) and are compensated by the adjacent layers as shown in the shifted layers representation. This brings the dipoles of neighbouring layers in close contact, giving the large stabilizing effect and the lowering of $\langle U^* \rangle$ in Table 1. Moving along the director from a molecule at the origin the neighbour on the dipole side is closer than that in the other direction (cf. Fig. 2D), explaining the split structure of the first $g(z)$ peak. At the same time the structure

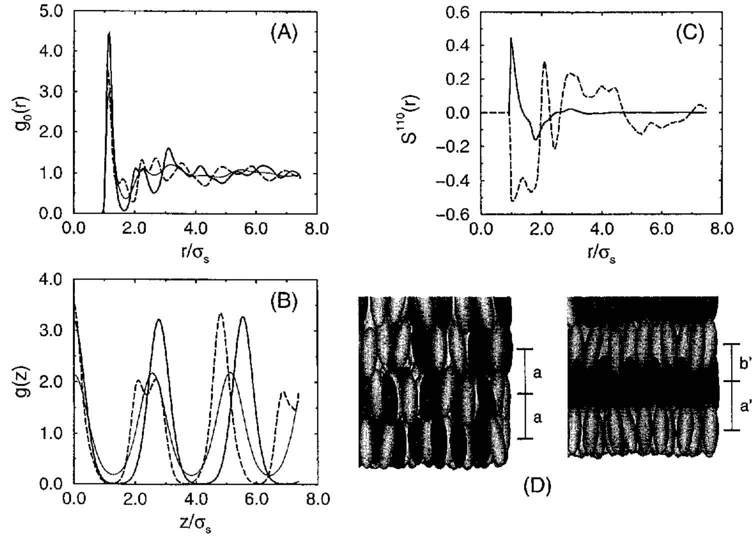

Fig. 2. The radial distribution $g_0(r)$, i.e. the probability, relative to the bulk one, of finding a second molecule at distance r from one chosen as origin (A), the density along the director $g(z)$ [9] (B), the angular correlation $S^{110}(r) = -(1/\sqrt{3})\langle[\hat{u}_1 \cdot \hat{u}_2]\rangle_r$ (C). The curves refer to dipole-less GB [9] (thin dotted), central (thick continuous) and shifted (dashed) dipoles. Plate (D) shows a side view of a fragment of the organization in the central (left) and shifted (right) dipole system, showing the repeat distances in $g(z)$.

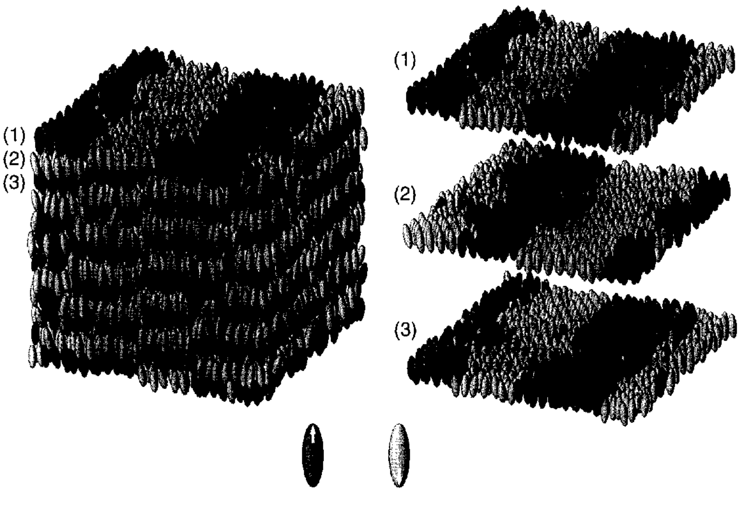

Fig. 3. The molecular organization (left) for the $N = 8000$ system with shifted dipoles, exhibiting the local polar domain pattern. The first three layers are exploded (right) to show how the domains are compensated antiferroelectrically by neighbouring layers.

is a S_A, without hexagonal order in the layer but with an interdigitation that shortens the wavelength of the density $g(z)$ (Fig. 2B). However, the organization is not a fully bilayer one, but has a stripe domain structure. This self-organizing ability is particularly striking and we have checked it in various ways. First we have simulated a much larger sample with $N = 8000$ and we notice at once that the same type of structure (see Fig. 3) is obtained in both cases. The calculations are particularly demanding and we have found it essential to use parallel computing techniques. For this sample size we have used a Cray T3D supercomputer with 64 (or 128) processors. We have coded a simple replicated data structure, where each processor, that has a copy of all the coordinates and executes exactly the same random number sequence, calculates the contribution of its subset of interactions to the energy of the trial move, employing standard shared memory (SHMEM) [18] and proprietary Cray routines. The $N = 8000$ sample was first prepared assembling $N = 1000$ equilibrated dipolar samples, then reequilibrated for around 50000 cycles. The total computer time is of the order of 100 months equivalent of a medium RISC workstation.

We have further tested the stability of this modulated structure versus a S_{A_2} performing yet another simulation with $N = 1000$, that was started from a bilayer prepared with dipoles up and down in alternate layers. We find that this configuration relaxes after about 80000 cycles to the stable stripe domain structure. The impression conveyed by the typical but instantaneous configurations in Figs. 1 and 3 of a different type of short range order in the central and shifted dipole systems can be substantiated calculating the angular correlation function [19] $S^{110}(r) = -(1/\sqrt{3})\langle[\hat{u}_1 \cdot \hat{u}_2]\rangle_r$, proportional to the average scalar product between the dipole of a molecule chosen as the origin and that of molecules at a distance r. This is plotted in Fig. 2C and shows clearly that the neighbour dipole is on average anti-parallel for the central and parallel for the shifted dipole molecules. At longer distances the situation is somewhat muddled by the layered structure, which means that molecules contributing to certain peaks could actually belong to different domains or different layers, but the short range order behaviour is unambiguous.

In conclusion, the problem of determining the collective organization of a system of dipolar molecules is definitely non-trivial, since it is the result of a balance between the tendency of two dipoles to arrange anti-parallel and the formation of domains with a common dipole orientation that, at least for two-dimensional systems, leads to fascinating domain structures [20,21]. Smectic phases obtained in real liquid crystals and in Gay-Berne models yield dipolar systems with a quasi two dimensional structure. We have shown by computer simulations that some of these molecular organizations follow from a simple polar Gay-Berne model of liquid crystals and that the position of the dipole in the molecule is important in establishing the structure. Large scale simulations, with sample size greater than the characteristic length of the domains, are essential in this respect and molecular resolution simulations like the present one should play a role in understanding these fascinating systems and as a help in the design of new mesophases.

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