

ATOMISTIC MODELLING OF FERROELECTRIC LIQUID CRYSTALS

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We have derived a detailed atomistic model for a compound exhibiting typical molecular features of ferroelectric liquid crystalline substances. We show that common general purpose forcefields like CHARMM need to be improved in order to reach an acceptable degree of accuracy. A generally applicable route to derive forcefield parameters using ab initio methods is introduced. First results of molecular dynamics simulations of smectic phases are reported.

Keywords: molecular dynamics simulations; ab initio calculations;
ferroelectric liquid crystals

INTRODUCTION

Molecular dynamics computer simulations proved to be rather useful for interpreting molecular behavior of nematic materials [1-5]. The most practically important mesogen derivatives, such as CB5, PCH5, CCH5 have been simulated. It has been shown that molecular conformation is strongly dependent on the phase state of the substance [4]. The existence of essentially anti-parallel alignment [1] of strongly polar mesogen molecules could not only be shown for the nematic state, but was also detectable

in the isotropic state. The success of realistic molecular dynamics (MD) simulations of nematic liquid crystals encouraged relevant studies of even more complex states. Recently a number of attempts were made to simulate ordering in chiral nematic [6] and smectic C* [7] phases. An explicit introduction of molecular flexibility and Coulomb-interactions enabled a detailed investigation of local molecular ordering in the nematic and isotropic phases of mesogens [8-9] and its comparison with experimental results. The necessity to shift from the use of model ellipsoids [10] to more realistic models represented by flexible site-site potentials is obvious for particularly molecule-dependent properties. Consequently, the need of 'realistic' interaction potentials as a fundamental basis for realistic simulations is without doubt. Therefore we used *ab initio* calculations in order to improve general purpose force-field parameters and to check their reliability. Our aim is to show an appropriate way to derive and refine atomistic potential functions for ferroelectric liquid crystalline compounds.

Object of our study is the chiral compound 4'-decyloxy-biphenyl-4 carboxylic acid 1-cyano-ethyl ester (10OBECE). 10OBECE does neither form a smectic, nor a nematic liquid crystal phase, but is used as a dopant in high spontaneous polarization mixtures. It's molecular features are that of typical ferroelectric liquid crystalline compounds (Fig.1). The absence of stable mesophases will enable us to study whether the MD-accessible time window is large enough to allow relaxation to thermodynamically stable states or whether the system is trapped close to the initial state.

A MODEL FOR FLC COMPOUNDS

Realistic state-of-the-art interaction potentials for moderately big molecules contain terms for electrostatic interactions, Pauli-repulsion, dispersion and terms representing intramolecular covalent forces. We used the functional form described in [11] for our model. The adequate description of the molecular electrostatic potential (ESP) is of great importance for the correct modelling of intra- and intermolecular interactions. The concept of atomic charge is a quite reasonable approach, combining a minimum of computational cost with an acceptable degree of accuracy; Especially useful for the case of molecular dynamics simulation facing large

systems. To represent the electrostatics adequately we decided to model the polar core of the molecule as an all-atom model, while the non-polar alkyl-chain is treated in the united atom approximation.

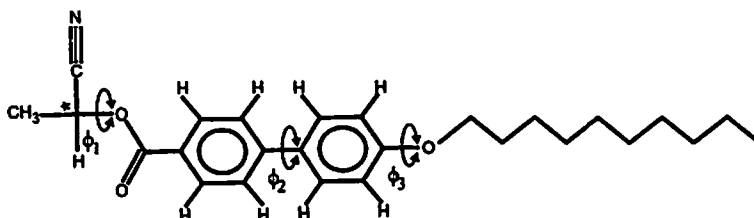


FIGURE 1 Model compound 10BECE. Ab initio potentials were derived for the indicated torsion angles.

The bonded and non-bonded interaction parameters for the core were taken from the Quanta 3.3 [12] parameter set, while the the alkyl-chain is represented by the improved OPLS-model of Smit et al. [13]. First, we obtained potential derived point charges based on ab initio calculations at the HF/6-31G** level of theory. The SCF-wavefunction of the energy minimized polar core (10BECE) was used for all electrostatic potential calculations.

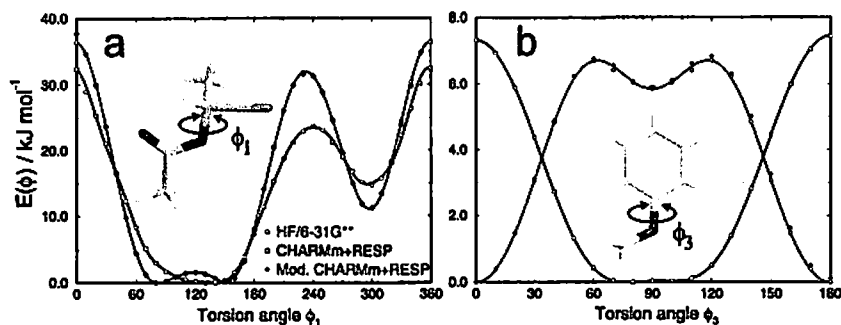


FIGURE 2 Original, ab initio and refined torsion potentials for ϕ_1 and ϕ_3 for depicted molecular fragments.

All quantumchemical calculations were done with GAUSSIAN 94. We performed fits restraining the fitted charges weakly to zero using the RESP-formalism described in [14]. Symmetry constraints for equivalent sites

were directly applied during the fit. The 1–4 Coulomb interactions were treated as in [11]. The atomic point charges reproduce the electrostatic potential at all relevant distances very well. At the distance of molecular contact (2 Å from the vdW-surface) the relative RMS deviation is 7.2 %. The accurate electrostatics in combination with a correct description of the torsion modes is essential for a correct representation of the accessible molecular configuration space. To check the forcefield parameterization we quantumchemically obtained fully relaxed torsion potentials for three strategic bonds (Fig. 1) from ab initio calculations of molecular fragments (two of them are shown in Fig. 2). These were taken as a reference for newly parameterized dihedral potentials. Up to 12 cosine terms had to be introduced to yield fits of appropriate quality. A comparison of the original (CHARMm+RESP) and refined (Mod. CHARMm+RESP) is given in Fig. 2. The refined model imitates exactly the HF/6-31G** data. Moreover, Fig. 2b shows clearly that this expensive procedure is justified. Instead of revealing an in-plane orientation, the alkyloxy-group equilibrium geometry of the uncorrected model is out of plane and therefore would totally fail to describe the real situation. The complete set of derived parameters and a more comprehensive description of the methods used will be given in [15].

MD SIMULATIONS

We perform classical molecular dynamics simulations using periodic boundary conditions. The Verlet-algorithm was employed to integrate Newton's equations of motion, while Berendsen's weak coupling was used to control temperature and pressure. To treat the long range interactions sufficiently accurate we applied the particle mesh Ewald (PME) method [16] with an approximate mesh spacing of 1 Å and 3rd-order b-spline interpolation. The Lennard-Jones interactions were truncated at a distance of 9 Å. Isotropic tail correction was used. All calculations were performed with the MOSCITO (<http://ganter.chemie.uni-dortmund.de/pas/moscito.html>) simulation package. The MD simulations were performed at 300 K and atmospheric pressure.

In order to prepare a possible smectic-type ordering we choose two distinct approaches which are shown in Fig. 3. In both cases an antiparallel alignment of molecules was realized in order to conserve C_2 symmetry. For the system which is referred to as 'BILAYER-system' (Fig. 3b), a non-classical setup has been chosen, which is formed by dimers stabilized by its strongly polar cyano groups. The main characteristic of the second system, which will be called 'FLC-system' (Fig. 3a), is a setup of overlapping cores. To avoid free volume the alkyl-chains have to penetrate the adjacent layers.

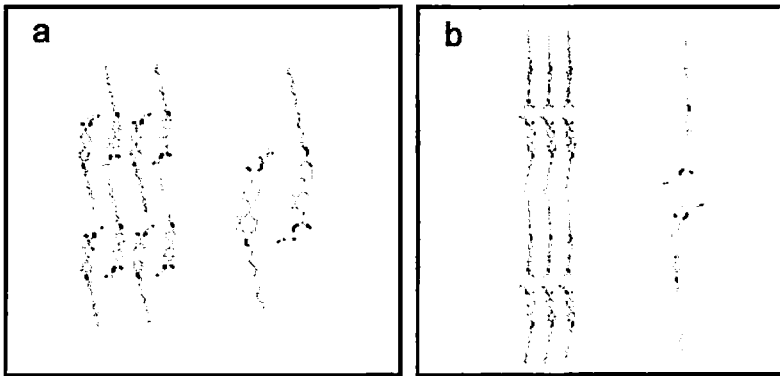


FIGURE 3 Initial system and dimer-configuration setup of the two systems studied. a) 'FLC'. b) 'BILAYER'.

For both systems small precursor systems of 32 (FLC) and 36 molecules (BILAYER) were created in order to generate a starting geometry. Both systems were run for 100 ps under constant temperature and pressure conditions. The box-lengths were allowed to fluctuate individually due to the corresponding pressure tensor components. After this initialization procedure both systems were duplicated in x and y directions. Each of the big systems (FLC:128 molecules; BILAYER:144 molecules) was then simulated for approximately 1.5 ns under similar conditions as described above

Both systems behave completely different although an equilibrium density of 1.04 g cm^{-3} is reached after a short initial relaxation time of about

300 ps. The first observation is that the FLC simulation box does not conserve its geometry during the simulation in contrast to the BILAYER system. While the density stays almost constant the box length in direction of the layer normal shrinks continuously.

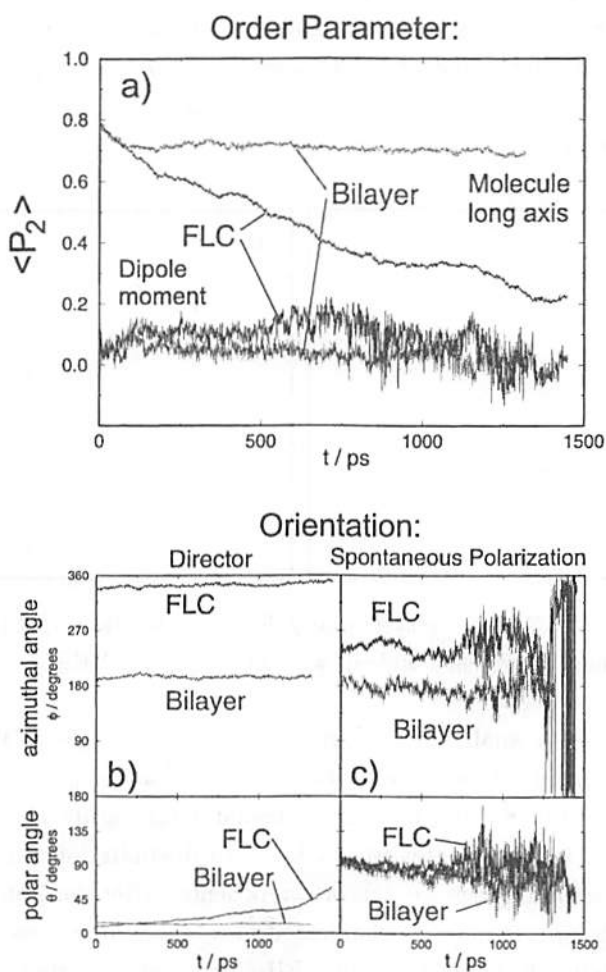


FIGURE 4 a) Time evolution of P_2 order parameters of both systems due to the molecular long axis and dipole moment. b) Time dependence of director and c) spontaneous polarization orientation.

FLC: The FLC system exhibits during the first 300 ps of relaxation a high diffusion coefficient in z-direction (almost 2 times higher than in perpendicular directions), indicating that molecular rearrangement is driven by repulsive intermolecular forces. A detailed analysis reveals that the chiral tails tend to be surrounded by the biphenyl fragments. The fast penetration of molecular alkyl tails into the hard core areas may lead to the dilution of smectic layers with alkyl moiety and finally causes the melting of the FLC sample. The orientational properties of the FLC-phase are remarkable. From the very beginning of the equilibration the molecules are spontaneously tilted and show a steady increase of the tilt during the simulation run (see Fig. 4b). The tilt-direction shows a small drift which could be expected keeping in mind the absence of any confinement or aligning fields. The permanent increase of the tilt angle and the absence of a noticeable saturation up to 45° at least indicates the system's instability. The lack of longitudinal spontaneous polarization is not surprising because of the antiparallel arrangement of molecules in the layers. In contrast, the appearance of a transversal component is remarkable. It remains in the plane of smectic layers and its direction does not change with the molecular tilt. This, in fact, was not artificially created, because the initial configuration's total dipole moment was aligned along the x-axis. The direction of the spontaneous polarization is fluctuating and remains almost perpendicular to the tilt plane, while the decreasing polar ordering as the simulation proceeds results in increased fluctuations of its orientation.

BILAYER: A completely different behavior can be observed for the BILAYER system. During the first 200 ps it shows a fast relaxation of all parameters (including simulation box dimensions) to afterwards stable values. It stays in a well defined layered smectic structure during the complete run. The system shows a quite realistic orientational ordering of the molecular long axis ($P_2=0.73$), to which it relaxes fast and which remains stable through the whole simulation. The average molecular long axis tilt angle is relatively small, exhibiting 13 to 15 degrees. The spontaneous

polarization for this system is non-zero and is oriented in the smectic plane. Interestingly, it coincides with the direction of the molecular tilt. This strange feature can be understood, keeping in mind that the molecular dipole moment has a rather big component parallel to the molecular long axis, while the dimer configuration (see Fig. 3b) eliminates a total transversal component. So, the observed total dipole moment is due to opposite tilt directions in different layers. The high spontaneous polarization of the very initial configuration is reduced several times during the relaxation period while the direction changes to become antiparallel to the x-axis. So, we can conclude that the spontaneous polarization is not due to non-relaxed orientation of the initial configuration. But, it is stabilized by an artificially created translational bilayered order which can not relax within the simulation time. Actually the system possesses the required attribute of the ferroelectric phase: a polar C_2 axis in the molecular tilt direction, parallel to smectic layers. In reality, of course, this is a metastable state, which should relax to the isotropic phase. Remarkable about this system is the fast initial relaxation to a metastable state, and that it is finally trapped herein. The relatively high diffusion coefficient of $1.3 \cdot 10^{-11} \text{ m}^2\text{s}^{-1}$ confirms that this phase is a liquid crystal.

CONCLUSIONS

It has been shown that a careful potential refinement based on *ab initio* studies is unavoidable, facing the fact that common forcefields were not especially optimized for LC compounds. We have elaborated methods which can do these calculations routinely. We can conclude from our simulations, that it is in principle possible to simulate ferroelectric liquid crystals in a meaningful manner. The molecules tilt spontaneously and their dipole moments are orientationally ordered. Nevertheless, one has to be aware that the simulated state depends strongly on initial conditions (smectic ordering, tilt angle). If the molecules are placed in an unfavorable initial configuration, the system may relax to any metastable phase (isotropic, nematic or crystal). A positive aspect is that despite the comparatively big molecular dimensions this process is completed in

several hundred picoseconds. Within this time not only relative molecular positions are equilibrated, but also properties such as molecular tilt and spontaneous polarization.

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