published as: C. Zannoni, Computer simulation and molecular design of model liquid crystals, in Chemistry at the beginning of the third Millennium: Molecular Design, Supramolecules, Nanotechnology and Beyond, L. Fabbrizzi and A. Poggi Eds., Springer-Verlag, 319-342 (2000)

Computer simulation and molecular design of model liquid crystals

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Abstract. In this chapter we discuss some of the problems and peculiarities of the computer simulation of liquid crystals and we briefly summarize the state of the art in the field.

1. Models for mesogenic molecules

Liquid crystals are anisotropic fluids characterized by a long range orientational order and by a reduced (like in smectics) or altogether absent (like in nematics) positional order of the constituent molecules [1,2]. The properties of liquid crystals in certain thermodynamic conditions critically depend on their long-range molecular organisation and on the proximity of an order-disorder phase transition. Here we shall be concerned with molecular level models that can be used to simulate liquid crystals and their properties. The most natural model for molecules that yield liquid crystals (mesogenic molecules), like for any other molecule, is probably an atomistic one, where each atom or small group of atoms (e.g. a CH) is represented by a suitable attractive -repulsive centre. A suitable force field between bonded and non bonded centres is chosen [3] and the molecular representation obtained (cf. Fig.1) is very close to chemical intuition.

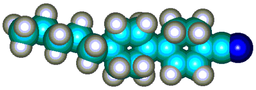

Fig. 1. An atomistic model of a typical mesogenic molecule: *trans*-4-(*trans*-4-n-pentylcyclohexyl) cyclohexylcarbonitrile (CCH5).

The simulation of the macroscopic properties and of the molecular organisation obtained for a system of N model molecules at a certain temperature and pressure (T, P) typically proceeds through one of the two current mainstream methods of computational statistical mechanics: molecular dynamics (MD) or Monte Carlo (MC) [4,5]. MD sets up and solves step by step the equations of motions for all the particles in the system and calculates properties from the time trajectories obtained. MC calculates instead average properties for the system from equilibrium configurations generated with an algorithm designed to generate sets of positions and orientations of the N molecules with a frequency proportional to their Boltzmann factor.

Both methods, although quite different, proceed through repeated evaluations of the energy and thus of the intermolecular interactions in the sample (as well as of their derivatives to evaluate forces, at least in MD). Two examples of the equilibrium configurations obtained are shown in Fig.2, for a system of N=98 CCH5 molecules at conditions typical of the nematic and isotropic state [6].

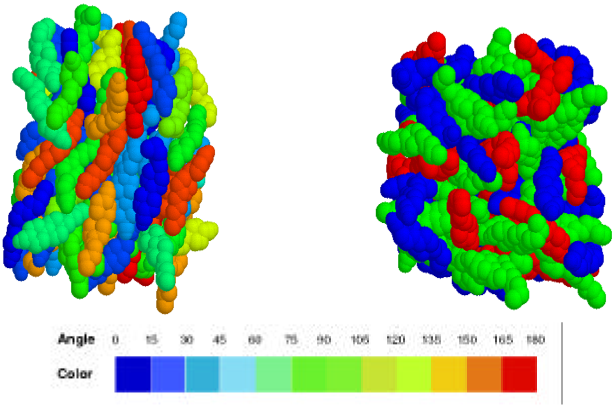

Fig. 2. A typical configuration of CCH5 molecules as obtained from molecular dynamics simulations in the isotropic phase at T= 380 K (right) and in the nematic at T=300 K (left). The colour indicates the molecular orientation from parallel (blue) to antiparallel (red) to the preferred orientation according to the palette shown [6].

However, one peculiarity of nematic liquid crystals is that while their local structure is essentially that of an ordinary liquid, they also exhibit orientational transitions: from nematic to isotropic, where they lose their long-range orientational order or from nematic to smectic, where they form layered structures The observation of such phase transitions requires fairly large samples, of hundreds of preferably more than a thousand molecules.

The problem with the atomistic type models is thus simply with the number of interacting centres they contain that rapidly takes the simulation beyond the range of current capabilities (see, however for overviews of recent progresses the contributions of Wilson, Glaser, Procacci in [5] and a review of Crain and Komolkin [7]).

One additional feature of liquid crystal simulations is that quite often we do not wish to investigate the detailed properties of a specific molecule, CCH5 say, that we already know to form a liquid crystal and whose structure we know. On the contrary we often have the problem of designing molecules that do not exist as yet! A typical problem could be the optimisation of the electric polarization properties of a liquid crystal formed of molecules containing a permanent dipole moment. The molecular design question could be posed as: what is the effect of changing the position, the orientation and the strength of the dipole on the structure of the liquid crystal phases obtained. In these cases it is essential to give up as many atomic details as possible and to consider lower resolution models where molecules are approximated with particles of simple shape. A simple choice often made is that of using purely repulsive models, e.g. hard spherocylinders or ellipsoids. This choice [8], which is consistent with the belief of many physicists [9] that it is only shape that determines the structure of a liquid and attractive for the relative simplicity of this type of models is more justified for ordered phases obtained with colloidal suspensions [10] then with the thermotropic materials we are interested with. Indeed in purely repulsive models [8] temperature plays no direct role, while the change from isotropic to nematic and then to smectic or crystal is temperature driven [1]. Moreover, although various ordered phases can be obtained, it is worth mentioning that no liquid - vapour transition is observed with purely repulsive models. We are thus particularly interested in considering simple molecular models, like the Gay-Berne potential [11] described in the following section, which are anisotropic but contain both an attractive and repulsive part.

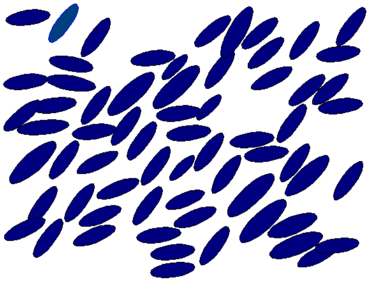

Fig. 3. A molecular level model of liquid crystals representing the molecules as ellipsoids

2. The Gay-Berne potential

The Gay-Berne (GB) potential in its uniaxial [11] and biaxial [12,13] version can be regarded as a generalized anisotropic and shifted version of the Lennard-Jones interaction commonly used for simple fluids [4], with attractive and repulsive contributions that decrease as inverse powers of distance:

$$U(r) = 4e\left[\left(\frac{s}{r}\right)^{12} - \left(\frac{s}{r}\right)^{6}\right]$$

(1

In the GB model the strength, ε, and the range, σ, parameters depend on the orientation vectors $\mathbf{u}_\mathrm{i}$, $\mathbf{u}_\mathrm{j}$ of the two particles and on their separation vector **r**. Here we show the uniaxial version for simplicity:

$$U(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\mathbf{r}) = 4e_0 e'^{m} e^{n}\left[\left(\frac{s_0}{r - s(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}}) + s_0}\right)^{12} - \left(\frac{s_0}{r - s(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}}) + s_0}\right)^{6}\right]$$

(2

where the cap indicates a unit vector, the anisotropic contact distance is

$$s(\mathbf{u}_i,\mathbf{u}_j,\mathbf{r}) = s_0\left\{1 - \frac{c}{2}\left[\frac{(\mathbf{u}_i\cdot\mathbf{r} + \mathbf{u}_j\cdot\mathbf{r})^2}{1 + (\mathbf{u}_i\cdot\mathbf{u}_j)c} + \frac{(\mathbf{u}_i\cdot\mathbf{r} - \mathbf{u}_j\cdot\mathbf{r})^2}{1 - (\mathbf{u}_i\cdot\mathbf{u}_j)c}\right]\right\}^{-1/2}$$

(3

and c is an anisotropy parameter related to the length $\sigma_{||}$ and the breadth $\sigma_{\perp}$ of the ellipsoid representing the molecule:

$$c = \frac{s_{\parallel}^{2} - s_{\perp}^{2}}{s_{\parallel}^{2} + s_{\perp}^{2}} . \qquad (4$$

Similarly the interaction anisotropy is the product of two terms:

$$e'^{m}(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j,\hat{\mathbf{r}}) = \left\{1 - \frac{c'}{2}\left[\frac{(\hat{\mathbf{u}}_i\cdot\hat{\mathbf{r}} + \hat{\mathbf{u}}_j\cdot\hat{\mathbf{r}})^2}{1+(\hat{\mathbf{u}}_i\cdot\hat{\mathbf{u}}_j)c'} + \frac{(\hat{\mathbf{u}}_i\cdot\hat{\mathbf{r}} - \hat{\mathbf{u}}_j\cdot\hat{\mathbf{r}})^2}{1-(\hat{\mathbf{u}}_i\cdot\hat{\mathbf{u}}_j)c'}\right]\right\}^{m} \qquad (5$$

$$e^{n}(\hat{\mathbf{u}}_i,\hat{\mathbf{u}}_j) = \left[1 - (\hat{\mathbf{u}}_i\cdot\hat{\mathbf{u}}_j)^2 c^2\right]^{-n/2} \qquad (6$$

where μ and ν, taken to be 2,1 in the original formulation [11,14-16], are parameters used to tune the shape of the potential and

$$c' = \frac{(e_s/e_e)^{1/m} - 1}{(e_s/e_e)^{1/m} + 1} \qquad (7$$

reflects the anisotropy in the potential well depths for the side-by-side and end- to-end configurations. Typical values used here for rod-like molecules (see Fig.1) are length to breadth $\sigma_{\parallel}/\sigma_{\perp}=3$ and well depth anisotropy $\varepsilon_{\perp}/\varepsilon_{\parallel}=5$. We also employ parameters $\mu=1$ and $\nu=3$ [17] that generate nematics with a wider temperature range than those in [11,13,14] and use σ_0, ε_0 as units of length and energy. Typical values for σ_0, ε_0 in real units could be $\sigma_0=\sigma_{\perp}=5$ Å, $\varepsilon_0/k=100$K.

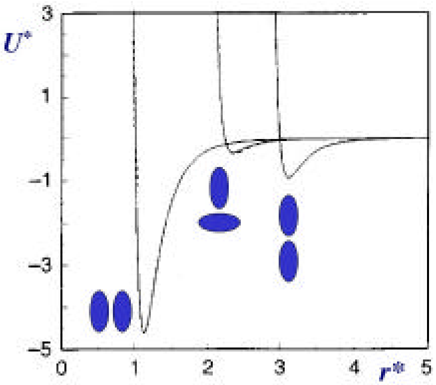

Fig. 4. Sections of the GB potential $U^*=U/\varepsilon_0$ with $\sigma_{\parallel}/\sigma_{\perp}=3$, $\varepsilon_{\perp}/\varepsilon_{\parallel}=5$ and energy parameters $\mu=1$ and $\nu=3$ [17] shown for side-by-side, tee and end-to-end orientations as a function of scaled distance $r^*=r/\sigma_0$.

The potential is strongly anisotropic and favours a side – side alignment, as we see from the few sections of the GB potential surface in Fig.4, but not to the point of necessarily giving a crystal when cooling from the isotropic phase. Although relatively simple to computer code the potential is already too complicated for a sufficiently accurate theoretical treatment and has to be studied using the numerical techniques of computer simulations. Indeed both Monte Carlo and Molecular Dynamics methods have been employed [5,13-16] to get the equilibrium phases generated by the GB potential under certain thermodynamic conditions and to construct at least in part its phase diagram. In Fig. 5 we show typical molecular organisations obtained for a system of $N=10^3$ GB particles using MC at a scaled density $\rho^*=0.3$ in the crystal, smectic B, nematic and isotropic phase [17]. We have colour coded the orientations of the molecules relative to the preferred direction of the liquid crystal (the director) as shown by the palette in Fig.5 to highlight orientational ordering.

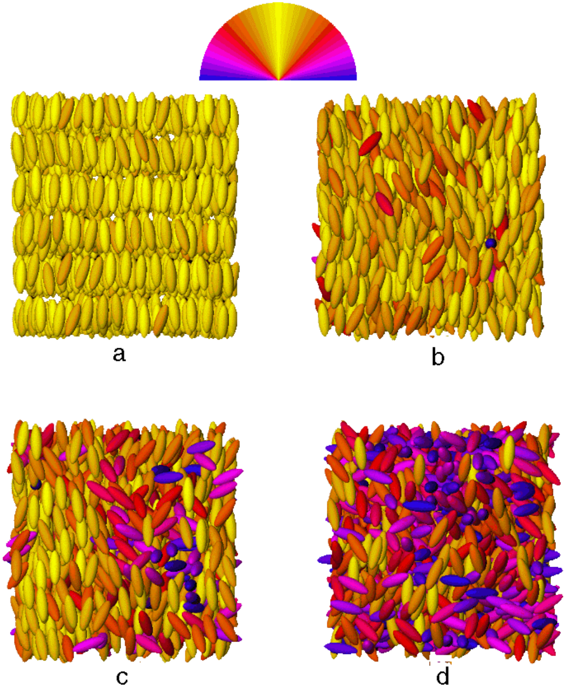

Fig. 5. Typical MC configurations of GB systems at four temperatures in the crystal (a), smectic B (b), nematic (c) and isotropic (e) phase. Details are given in [17].

We see that the GB phases have the expected characteristics: in the isotropic phase all orientations (and thus all colours) are represented; the nematic shows a dominance of molecules parallel to the director (yellow here), but no positional order. Cooling further gives smectic layering and eventually crystal like three dimensional order.

Gay-Berne models can also be used to study the order of a liquid crystal close to a certain phase transition and to answer some basic questions, e.g. about the alignment at that interface.

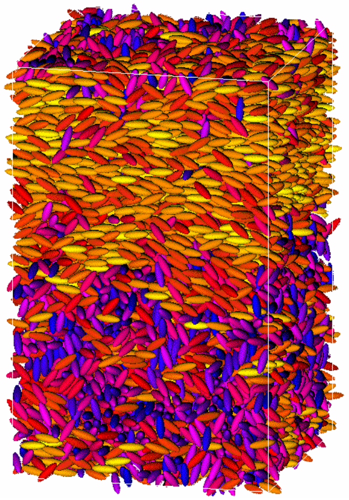

Fig. 6. A typical configuration for the GB model at the nematic-isotropic transition, showing that the molecules in the nematic phase coexisting with the isotropic one are aligned parallel to the interface[18].

In Fig.6 we show as an example the molecular organisation at the nematic-isotropic coexistence [18] that was obtained with a specially developed MD where the two halves of the cell containing N=12960 molecules are separately thermostated at temperatures slightly above and below the transition temperature. It is apparent that in this case molecules align parallel to the interface. Experimentally this is what happens, at least for some liquid crystals like n-(4 methoxy benzylidene)-4'-n Butyl aniline (MBBA), although other types of alignment are also found for other materials.

The GB system has also been shown to give a nematic -vapour transition, at least when its parameters are changed to $\mu=1$ and $\nu=1$ [19]. Also in this case molecules at the phase interface tend to be aligned parallel to it. Experimentally various types of behaviour are found at a free interface: e.g. planar for 4,4'-dimethoxy azoxy benzene (PAA) and perpendicular in cyanobiphenyls (see refs. in [19,20]). A perpendicular alignment was also observed for a GB system with shorter particles with $c= 2$ and $c'=5$, $\mu=1$, $\nu=2$ [20]. Apart from the basic transition properties, a number of physical observables have been determined for GB systems, including viscosity [21], elastic constants [22], thermal conductivity and diffusion coefficients [23], pretransitional properties [24]. The interaction of GB liquid crystals with surfaces to investigate the details of anchoring and structuring has been explored both for generic [25,26] and specific substrates like graphite [27]. Very large GB systems (over 80000 molecules) have also been recently studied to investigate some of the distinctive features of liquid crystals: topological defects [28,29], until now simulated only with lattice models [30].

In general the simple GB potential has proved able to yield the main liquid crystal phases and properties and thus to constitute an attractive reference potential for investigating trends of variation in the order and organisation of the nematic and smectic phases upon switching on of additional specific contributions. In the next section we shall see some examples of this approach.

Dipolar systems

We consider as an example the effect of changing molecular dipole position and orientation on the overall organisation of the dipoles in a liquid crystal phase. This is not only of academic interest in view of the current efforts to obtain fluid ferroelectric liquid crystals, that would be of great technological importance and that, although not theoretically forbidden, have until now eluded the efforts of synthetic chemists [31]. Notice that a ferroelectric arrangement of dipoles would correspond to a somewhat non-intuitive overall polar phase, with dipoles pointing in the same direction.

The pair potential we consider is simply a sum of the previously seen Gay - Berne interaction and of a dipolar term:

$$U_{mm}(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}_d) = \frac{m_i^* m_j^*}{r_d^{\,3}} \left[\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j - 3(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{r}}_d)(\hat{\mathbf{u}}_j \cdot \hat{\mathbf{r}}_d) \right] \qquad (8$$

where $\mathbf{r}_d$ is the vector joining the point dipoles m_i and m_j on the two molecules. In particular we consider [32] shifting an axial dipole from the centre to a position $d^*=d/\sigma=1$ towards the end of the molecule (see Fig.7). We consider a dipole strength $\mu^*=2$ in reduced units, which would correspond to about 2.4D in real units. While the preferred orientation of two dipoles at a certain distance and orientation can be easily guessed to be antiparallel, it is important to stress that the equilibrium organisation of a system of N polar molecules at a certain density and temperature cannot be reliably predicted without the use of computer simulations that can optimise the positions and orientations of all the N molecules at the same time.

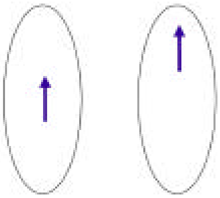

Fig. 7. A sketch of the central (left) and shifted (right) permanent dipole location in the two systems considered.

Thus if we start from the same density ρ*=0.30 used in the previous section for the apolar GB system and we confine ourselves to the smectic phase, we find from MC simulations of N=1000 dipolar particles that the central dipole system behaves as we might have expected, with an essentially random distribution of up and down dipoles in each layer and with little interdigitation. On the other hand the simulation of the shifted dipole system gives the surprisingly very different dipole organisation shown in Fig. 8.

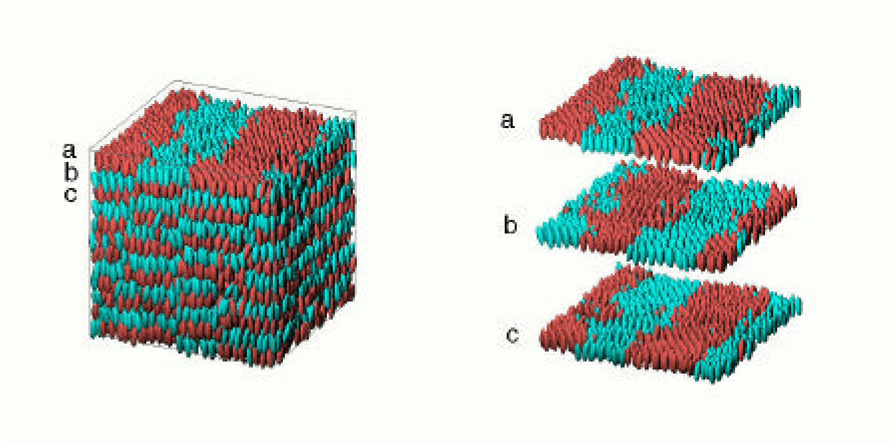

Fig. 8. The molecular organisation (left) for the N=8000 GB system with shifted axial dipoles, exhibiting the local polar domain pattern. The first three layers are exploded (right) to show how the domains are compensated anti - ferroelectrically by neighbouring layers. Red and blue indicate dipole up or down [32].

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 interdigitation and a large stabilising effect and the lowering of the energy. However, the organisation is not a fully bilayer one, but has a stripe domain structure. This self-organising ability is particularly striking and we have checked it in various ways and in particular simulating a much larger sample with N=8000 and verifying that the same type of structure (the one actually shown in Fig. 8) is obtained in both cases. It is worth noticing that even for these relatively simple systems the calculations are particularly demanding. Indeed, because of the long range nature of the dipolar interactions that are evaluated using the Ewald summation technique whose demand of computer time grows as $O(N^{3/2})$, we have found essential to use parallel computing techniques.

It is interesting to observe that these dipolar domain structures have been found experimentally by Levelut et al. [33] in rather complex liquid crystal mixtures. The simple model above helps to single out a design feature that favours the domain formation. This is particularly interesting from the perspective of trying to optimise the position of the dipole towards the formation of a ferroelectric phase [31]. Changes of dipole strength also have a significant effect and in particular increasing the dipole strength gives rise to the strongly interdigitated partial bilayer phase [1] observed experimentally and called smectic A_d [34].

Although here we have only briefly recalled the case of axial dipoles, the effect of changing the orientation of the dipole from axial to transversal has also been studied and shown to produce interesting dipole chain structures in the plane perpendicular to the director [35], as also observed in hard spherocylinders with a central transverse dipole [36].

Discotic systems

The essential requirement for the formation of liquid crystal phases is that of having non spherical molecular shapes. Although historically anisotropic phases have been obtained from elongated molecules, in the last twenty years flat, discotic, molecules have been shown to yield interesting nematic and columnar organisations and these discotics [1] form one of the most rapidly growing and important family of liquid crystals [37]. The typical structure of a discotic is that of a flat aromatic core, e.g. triphenylenes, truxenes, superyines and many other moieties have been employed, with a certain number of chains attached [1,37]. Another interesting possibility is that offered by metallorganic compounds, where a suitable transition metal helps in organising a set of ligands with an appropriate nearly planar geometry [38,39].

Here we consider a simple case of this kind, that of discs with an axial permanent dipole in the centre to examine their overall molecular and dipolar organisation. Structures resembling this exist for instance in polar discotic metallomesogens based on vanadyl 1,3-diketonate complexes [39] that have a large dipole moment normal to the plane of the molecule and have been found to give columnar phases. These systems are of particular interest as candidate for uniaxial ferroelectric phases, as an hexagonal structure of polar columns is expected to be globally ferroelectric, since the symmetry of the column lattice would not allow a cancellation of the dipoles of each stack of discs.

Despite the growing importance of discotic systems the number of computer simulations has been relatively small. Here we shall model the discotic mesogen using again a Gay Berne attractive-repulsive potential with an added dipole. We shall then employ Monte Carlo (MC) simulations to obtain the resulting equilibrium molecular organisation at a few selected temperatures.

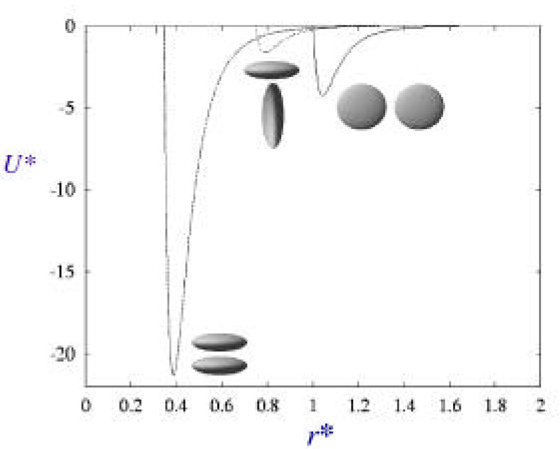

Fig. 9. Gay-Berne potential for discotic molecules with $\sigma_{\|}/\sigma_{\perp} = 0.345$, $\varepsilon_{\|}/\varepsilon_{\perp} = 5$ and energy parameters $\mu = 1$ and $\nu = 3$.

It is worth pointing out that although the GB systems we have discussed until now were made of elongated particles, the GB model can actually be used equally successfully for discotic particles, just utilizing oblate rather than prolate ellipsoid parameters [40]. The example considered here utilises a parameterisation related to that used by Emerson *et al.* in [40] and originally based on the dimensions of a triphenylene core, namely: shape and well depth anisotropy $\sigma_{\|}/\sigma_{\perp} = 0.345$ and $\varepsilon_{\|}/\varepsilon_{\perp} = 5$, but using instead energy parameters $\mu = 1$ and $\nu = 3$ [41]. We have studied a system of $N = 10^3$ discotic particles with central axial dipole using Monte Carlo computer simulations and we have shown that it gives isotropic, nematic and hexagonal columnar liquid crystal phases (see Fig.10), differently from the parameterisation [40] that yielded a tetragonal arrangement of columns. The system is then similar to the one studied experimentally, which was however not really ferroelectric. We have determined the overall polarization in our system and found that it is also not ferroelectric. Although this is somewhat disappointing we can however investigate why. We have thus also determined the molecular and dipolar distributions and the length of the polar domains in the columns [41]. At low temperature each column contains aligned dipolar domains but, as we can also see from Fig.10, we did not find fully polarized columns.

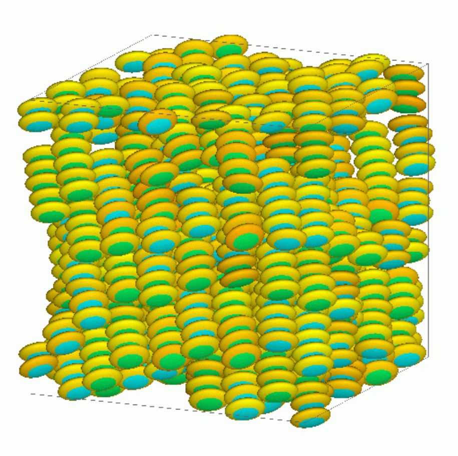

Fig. 10. A GB discotic liquid crystal with axial dipole in the columnar phase (at T * = 2.0). The green and cyan spots are used to distinguish head from tail of the molecular dipoles[41].

The typical length of each polar domain is less than ten molecules and the lack of consistent polarization of each column seems to be at the origin of the problem of lack of global phase polarization.

Conclusions

The molecular modelling problem that has often to be tackled in liquid crystals is that of designing molecules that have not yet been synthesised and that are able to yield mesophases with specific properties of interest for applications (such as ferroelectricity) rather than that of calculating in detail the properties of already known molecules. The simulation of model systems based on simple, molecular level, rather than atomistic, intermolecular potentials allows the identification of some of the physical features (e.g. molecular shape and attractive interaction anisotropy, biaxiality, electrostatic moments etc.) responsible of a certain collective behaviour, providing useful guidelines for the design of novel mesogenic molecules.

In this chapter we have presented a brief overview of recent results for systems of particles interacting with model potentials based on the Gay-Berne (GB) molecular level interaction that has shown to be a useful tool for studying nematic, smectic and columnar liquid crystals and we have presented and summarised the results of various examples of dipolar systems.

More complex molecular structures can be simulated by suitable combination of various ellipsoidal Gay-Berne and spherical Lennard-Jones particles e.g. to attempt modelling asymmetric molecules [42,43] or to include flexible chains[44]. Equally well other specific contributions, e.g. modelling quadrupolar [45] or hydrogen bond interactions could be added to the basic GB system [46]. With the continuous growth in computer resources it seems very likely that the level of detail and the feasibility of large scale molecular modelling will correspondingly continue to increase and to provide a useful tool for understanding complex behaviour in liquid crystals in terms of molecular features.

Acknowledgements

I should like to thank University of Bologna, MURST (PRIN *Cristalli Liquidi*), CNR PF and NEDO (Japan) for their financial support to our work and R. Berardi, S. Boschi, A. Emerson, L. Muccioli, S. Orlandi, A. Porreca, P. Pasini for their contributions to the work described here.

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